

ASSESSMENT REPORT ON
ARSENIC
FOR DEVELOPING
AMBIENT AIR QUALITY
OBJECTIVES



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FOR DEVELOPING AN AMBIENT AIR QUALITY OBJECTIVES**

**Prepared by
WBK & Associates Inc.**

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FOREWORD

Alberta Environment maintains Ambient Air Quality Objectives¹ to support air quality management in Alberta. Alberta Environment currently has ambient objectives for more than thirty substances and five related parameters. These objectives are periodically updated and new objectives are developed as required.

With the assistance of the Clean Air Strategic Alliance, a multi-stakeholder workshop was held in October 2000 to set Alberta's priorities for the next three years. Based on those recommendations and the internally identified priority items by Alberta Environment, a three-year work plan ending March 31, 2004 was developed to review four existing objectives, create three new objectives for three families of substances, and adopt six new objectives from other jurisdictions.

In order to develop a new three-year work plan, a multi-stakeholder workshop was held in October 2004. This study was commissioned in preparation for the workshop to provide background information on alternative, science based, and cost effective methods for setting priorities.

This document is one of a series of documents that presents the scientific assessment for these adopted substances.

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¹ **NOTE:** The *Environmental Protection and Enhancement Act*, Part 1, Section 14(1) refers to "ambient environmental quality objectives" and uses the term "guidelines" in Section 14(4) to refer to "procedures, practices and methods for monitoring, analysis and predictive assessment." For consistency with the *Act*, the historical term "ambient air quality guidelines" is being replaced by the term "ambient air quality objectives." This document was prepared as the change in usage was taking place. Consequently any occurrences of "air quality guideline" in an Alberta context should be read as "air quality objective."

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TABLE OF CONTENTS

FOREWORD.....	i
ACKNOWLEDGEMENTS.....	ii
LIST OF TABLES.....	v
LIST OF FIGURES.....	v
SUMMARY.....	vi
 1.0 INTRODUCTION.....	 1
2.0 GENERAL SUBSTANCE INFORMATION.....	2
2.1 Physical and Chemical Properties.....	2
2.2 Emission Sources and Ambient Levels.....	2
2.2.1 <i>Natural Sources</i>	2
2.2.2 <i>Anthropogenic Sources</i>	2
2.2.3 <i>Ambient Levels</i>	7
3.0 ATMOSPHERIC CHEMISTRY AND FATE.....	8
4.0 EFFECTS ON HUMANS AND ANIMALS.....	9
4.1 Overview of Chemical Disposition.....	9
4.2 Genotoxicity.....	10
4.3 Acute Effects.....	11
4.3.1 <i>Acute Human Effects</i>	11
4.3.2 <i>Acute and Sub-Acute Animal Effects</i>	11
4.3.2.1 Respiratory Effects.....	12
4.3.2.2 Developmental Effects.....	14
4.3.2.3 Carcinogenic Effects.....	14
4.3.2.4 Other Effects.....	14
4.4 Chronic Effects.....	15
4.4.1 <i>Chronic Human Effects</i>	15
4.4.1.1 Respiratory Effects.....	15
4.4.1.2 Vascular and Cardiovascular Effects.....	15
4.4.1.3 Neurological Effects.....	17
4.4.1.4 Developmental Effects.....	18
4.4.1.5 Carcinogenic Effects.....	18
4.4.1.6 Other Effects.....	19
4.4.2 <i>Chronic Animal Effects</i>	19
4.5 Summary of Adverse Health Effects of Arsenic Inhalation.....	19
5.0 EFFECTS ON MATERIALS.....	20
6.0 AIR SAMPLING AND ANALYTICAL METHODS.....	21
6.1 Introduction.....	21
6.2 Sampling Methods.....	21

6.2.1	<i>Hi-Vol Sampler</i>	21
6.2.2	<i>Dichotomous Sampler</i>	22
6.2.3	<i>Partisol Sampler</i>	22
6.2.4	<i>Alternative Sampling Methods</i>	23
6.3	Analytical Methods	23
6.3.1	<i>Atomic Absorption Spectroscopy</i>	24
6.3.2	<i>X-Ray Fluorescence Spectroscopy</i>	24
6.3.3	<i>Inductively Coupled Plasma Spectroscopy</i>	25
6.3.4	<i>Inductively Coupled Plasma/Mass Spectroscopy</i>	25
6.3.5	<i>Proton Induced X-Ray Emission Spectroscopy</i>	25
6.3.6	<i>Instrumental Neutron Activation Analysis Spectroscopy</i>	26
6.3.7	<i>Alternative Analytical Methods</i>	26
7.0	AMBIENT GUIDELINES	29
7.1	Arsenic Air Quality Guidelines	29
7.1.1	<i>Canada</i>	29
7.1.2	<i>United States</i>	51
7.1.3	<i>International Agencies</i>	51
8.0	RISK CHARACTERIZATION	53
8.1	Relevant Chemical Forms	53
8.2	Exposure Assessment	53
8.3	Toxicity Assessment	53
8.4	Characterization of Risk	54
9.0	REFERENCES	56

LIST OF TABLES

Table 1	Identification of Arsenic and Select Arsenic Compounds (Genium, 1999)	3
Table 2	Physical and Chemical Properties of Arsenic and Select Arsenic Compounds ^a	4
Table 3	Emissions of Arsenic and its Compounds According to NPRI, 2002 (in tonnes).....	5
Table 4	Common Inorganic Arsenic Compounds ^a	9
Table 5	Examples of NOAELs and LOAELs Associated with Acute Arsenic Inhalation (Experimental Animals).....	12
Table 6	Examples of NOAELs and LOAELs Associated with Sub-Acute Arsenic Inhalation (Experimental Animals).....	13
Table 7	Examples of NOAELs and LOAELs Associated with Chronic Arsenic Inhalation (Human).....	16
Table 8	Method Advantages and Disadvantages	28
Table 9	Summary of Air Quality Guidelines for Arsenic	52

LIST OF FIGURES

Figure 1	Range of Air Quality Guidelines for Arsenic Proposed by Various Agencies for Protection of Human Receptors	55
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SUMMARY

Arsenic is an element that exists in several oxidation states: -3, 0, +3 or +5. It occurs naturally in the earth's crust, associated with igneous and sedimentary rocks in the form of sulfide, arsenide, and sulfarsenide compounds, or in the form of oxides or arsenates. Arsenic can also combine with hydrogen and carbon to form organic arsenic compounds.

Arsenic and its compounds are used in a number of applications and industrial processes. Arsenic trioxide is used as a starting product for many arsenic compounds. Chrome copper arsenate is used as a wood preservative. Other uses of arsenic and its compounds include the manufacturing of glass, metallurgy, the manufacturing of gallium arsenide for the electronics industry and some medical applications. The industrial sectors contributing the most to arsenic emissions in Canada are the metal smelting and refining sector and the power and electrical utilities sector. In Alberta, the power and electrical utilities sector as well as the wood industry (wood preserving) contribute to arsenic emissions.

Most arsenic released into the atmosphere is associated with fine particles ($<2\text{ }\mu\text{m}$), usually in the form of arsenate (+5 oxidation state) and arsenite (+3 oxidation state). The processes governing the fate of arsenic in the atmosphere are the same processes that govern the transport and removal of these small particles from the atmosphere.

Sub-acute female mice exposures to arsenic trioxide at $20,000\text{ }\mu\text{g As/m}^3$ for 6 hours/day and 7 days/week for 14 days are reported to cause severe respiratory problems possibly due to exposure to particulates, not necessarily due to arsenic toxicity. Sub-acute female mice exposures to trivalent arsenic at $120\text{ }\mu\text{g As/m}^3$ for 3 hours are also reported to increase susceptibility to respiratory pathogens, indicating a potential immune system effect.

Chronic (low-level, long-term) human exposures in the workplace are reported to result in: irritation of the respiratory tract (0.5 to 50 year exposure to arsenic trioxide at $610\text{ }\mu\text{g As/m}^3$); cardiovascular effects (average 23 exposure to arsenic trioxide at $360\text{ }\mu\text{g As/m}^3$); neurological effects (28 year exposure to arsenic trioxide at $310\text{ }\mu\text{g As/m}^3$); severe dermatitis (0.5 to 50 year exposure to arsenic trioxide at $610\text{ }\mu\text{g As/m}^3$); and increased risk of lung cancer (0.25 to 30 year exposure to arsenic trioxide at 70 to $210\text{ }\mu\text{g As/m}^3$). Humans appear to be more sensitive to chronic arsenic toxicity than many laboratory animals. Carcinogenicity has not been demonstrated in animal studies.

The majority of trace metals present in ambient air, including arsenic, are particle-bound. Sample collection schemes suitable for collection of trace metals follow methods appropriate for particulate matter measurement. Many analytical methods exist to characterize trace metals and each has its own advantages and disadvantages.

Urban settings – in which most air quality data are available for – are settings with higher metal concentrations in ambient air compared to rural settings. Ambient air data in central Edmonton and central Calgary are available for the period June 1991 to November 2000. Median and maximum arsenic concentrations associated with $\text{PM}_{2.5}$ in ambient air were <0.0001 and $0.003\text{ }\mu\text{g/m}^3$ (central Edmonton) and <0.0001 to $0.0059\text{ }\mu\text{g/m}^3$ (central Calgary).

1.0 INTRODUCTION

Alberta Environment establishes Ambient Air Quality Guidelines under Section 14 of the Environmental Protection and Enhancement Act (EPEA). These guidelines are part of the Alberta air quality management system (AENV, 2000).

The main objective of this assessment report was to provide a review of scientific and technical information to assist in evaluating the basis and background for an ambient air quality guideline for arsenic. The following aspects were examined as part of the review:

- physical and chemical properties,
- existing and potential anthropogenic emissions sources in Alberta,
- effects on humans, animals, vegetation, and materials,
- ambient air guidelines in other Canadian jurisdictions, United States, World Health Organization and New Zealand, and the basis for development and use,
- characterization of risks to exposed receptors,
- monitoring techniques.

Important physical and chemical properties that govern the behaviour of arsenic in the environment were reviewed and presented in this report. Existing and potential anthropogenic sources of arsenic emissions in Alberta were also presented. Anthropogenic emissions are provided in Environment Canada's National Pollutant Release Inventory (NPRI).

Scientific information about the effects of arsenic on humans and animals is reported in published literature and other sources. This information includes toxicological studies published in professional journals and reviews and information available through the US Agency for Toxic Substances and Disease Registry (ATSDR) and US Environmental Protection Agency's Integrated Risk Information System (IRIS). These sources provided valuable information for understanding health effects of arsenic exposure.

Ambient air guidelines for arsenic are used by numerous jurisdictions in North America for different averaging-time periods. These guidelines can be developed by using an occupational exposure level and dividing it by safety or adjustment factors, using cancer risk assessment procedures, or by using non-cancer risk assessment procedures. Examples of cancer and non-cancer risk assessment procedures are provided in WBK (2003). The basis for how these approaches are used by different jurisdiction to develop guidelines was investigated in this report.

Accurate measurement of trace metals, including arsenic, in ambient air is often difficult in part because of the variety of substances, the variety of potential techniques for sampling and analysis, and the lack of standardized and documented methods. The United States Environmental Protection Agency (US EPA), National Institute of Occupational Safety and Health (NIOSH), and Occupational Safety and Health Administration (OSHA) are the only organizations that provide documented and technically reviewed methodologies for determining the concentrations of selected trace metals of frequent interest in ambient and indoor air. These methods, which are generally accepted as the preferred methods for trace metal sampling and analysis, were reviewed and presented in this report.

2.0 GENERAL SUBSTANCE INFORMATION

Arsenic (As) exists in several oxidation states: -3, 0, +3 or +5 (Lide, 2002). Elemental arsenic occurs as one of two forms: yellow and gray (or metallic) arsenic with gray arsenic being more stable (Lide, 2002). Arsenic occurs naturally in the form of sulfides, arsenides, sulfarsenides or in the form of oxides or arsenates (Lide, 2002). Arsenic can combine with oxygen, chlorine or sulphur to form inorganic arsenic compounds or it can combine with hydrogen and carbon to form organic arsenic compounds (ATSDR, 2000).

Arsenic and its compounds are used in a number of applications and industrial processes. Compounds of importance include arsenic trioxide (As_2O_3), arsenic sulphides, Paris green ($3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$), calcium arsenate and lead arsenate (Lide, 2002). Arsenic trioxide is used as a starting product for many arsenic compounds (Genium, 1999). Calcium arsenate and lead arsenate were, in the past, used as insecticides but have since been replaced by organic pesticides (ATSDR, 2000). Some organic and inorganic arsenic compounds were also used as herbicides (ATSDR, 2000). Chrome copper arsenate (CCA) is used as a wood preservative (ATSDR, 2000). Other uses of arsenic and its compounds include the manufacturing of glass, metallurgy, the manufacturing of gallium arsenide for the electronics industry and some medical applications (Genium, 1999).

Table 1 provides a list of important identification numbers and common synonyms for arsenic and select arsenic compounds.

2.1 Physical and Chemical Properties

The physical and chemical properties of arsenic and select arsenic compounds are summarized in Table 2.

2.2 Emission Sources and Ambient Levels

2.2.1 Natural Sources

Arsenic occurs naturally in the earth's crust, associated with igneous and sedimentary rocks in the form of inorganic arsenic (Tamaki and Frankenberger cited in ATSDR, 2000). Weathering of these rocks can lead to the formation of wind blown dust, a source of arsenic in the atmosphere (ATSDR, 2000). Other natural sources of arsenic include volcanic eruptions, volatilization of methylarsines from soil (ATSDR, 2000; Chilvera and Peterson cited in CEPA, 1993), sea salt sprays and forest fires (ATSDR, 2000).

2.2.2 Anthropogenic Sources

Table 3 presents emissions of arsenic according to Environment Canada's 2001 National Pollutant Release Inventory (NPRI, 2002). According to Table 3, the industrial sectors contributing the most to arsenic emissions in Canada are the metal smelting and refining sector

Table 1 Identification of Arsenic and Select Arsenic Compounds (Genium, 1999)

Property	Arsenic	Arsenic Acid	Arsenic Pentoxide	Arsenic Trioxide
Chemical Formula	As	AsH ₃ O ₄	As ₂ O ₅	As ₂ O ₃
Chemical Structure	As	$ \begin{array}{c} \text{OH} \\ \\ \text{HO}-\text{As}-\text{O} \\ \\ \text{OH} \end{array} $	$ \begin{array}{c} \text{O} \\ \\ \text{O}-\text{As}-\text{O} \\ \quad \quad \\ \text{O} \quad \text{O} \quad \text{O} \end{array} $	$ \begin{array}{c} \text{O} \\ \\ \text{O}-\text{As}-\text{O} \\ \quad \quad \\ \text{O} \quad \text{O} \quad \text{O} \end{array} $
CAS Registry number	7440-38-2	7778-39-4	1303-28-2	1327-53-3
RTECS number	CG0525000	CG0700000	CG2275000	CG3325000
UN Number	UN1558	UN1553	UN1559	UN1561
Common Synonyms and Tradenames	Arsen Arsenia Arsenic - 75 Arsenic black Arsenicals Colloidal arsenic Gray arsenic Metallic arsenic	Arsenate Crab grass killer Dessicant L-10 Hi-Yield Dessicant H-10 Orthoarsenic acid Scorch Zotox Zotox crab grass killer	Arsenic acid anhydride Arsenic anhydride Arsenic (V) oxide Arsenic oxide Arsenic pentaoxide Diarsenic pentoxide	Arsenic (III) oxide Arsenic oxide Arsenic sesquioxide Arsenic (III) oxide Arsenicum album Arsenigum saure Arsenious acid Arsenious acid anhydride Arsenite Arsenolite Arsenous acid Arsenous acid anhydride Arsenous oxide Arsenous oxide anhydride Arsentrioxide Arsodent Claudelite Claudelite Crude arsenic Diarsenic trioxide White arsenic

Table 2 Physical and Chemical Properties of Arsenic and Select Arsenic Compounds^a

Property	Arsenic	Arsenic Acid	Arsenic Pentoxide	Arsenic Trioxide
Molecular Weight (g/mol)	74.922	141.944	229.840	197.841
Oxidation State	0	+V	+V	+III
Physical state	gray metal	exists only in solution white translucent crystals ^b ; very pale yellow syrupy liquid (commercial grade) ^b	white amorphous powder	white cubic crystals (arsenolite) white monoclinic crystals (claudetite)
Melting Point (°C)	817 (triple point at 3.7 MPa)	35.5 ^b	315	274 (arsenolite) 313 (claudetite)
Boiling Point (°C)	603 (sublimation point)	160 ^b	No data	460
Density (g/cm ³)	5.75	2.2 (specific gravity at 20°C) ^b	4.32	3.86 (arsenolite) 3.74 (claudetite)
Specific gravity (gas) (air = 1)	no data	no data	no data	no data
Vapour pressure	1 mm Hg at 372°C ^b	no data	no data	66.1 mm Hg at 312°C ^b
Solubility in water	insoluble in water	302 g/100 cm ³ at 20°C ^b	65.8 g/100 g H ₂ O at 20°C; combines very slowly with water ^b	2.05 g/100 g H ₂ O at 20°C
Solubility in other solvents	insoluble in caustic and nonionizing acids ^b	freely soluble in glycerol ^b	very soluble in ethanol soluble in acid and alkali ^b	soluble in dilute acid solutions, alkaline solutions; insoluble in ethanol
Henry's Law Constant (atm.m ³ /mol)	no data	no data	no data	no data
Octanol water partition coefficient (log K _{ow})	no data	no data	no data	no data
Organic carbon partition coefficient (Log K _{oc})	no data	no data	no data	no data
Odour threshold (mg/m ³)	odourless ^b	no data	odourless ^b	odourless ^b
Bioconcentration factor in fish (log BCF)	no data	no data	no data	no data
Conversion factors for vapour (at 25 °C and 101.3 kPa)	no data	no data	no data	no data

^a all data from Lide, 2002 unless otherwise indicated

^b Genium, 1999

Table 3 Emissions of Arsenic and its Compounds According to NPRI, 2002 (in tonnes)

NPRI ID	Company	City	Province	Emissions of Arsenic and its Compounds (tonnes)			
				Air	Water	Land	Underground Total
3623	Noranda Inc	Rouyn-Noranda	QC	98,060	0.254	0.000	98,314
3992	Nova Scotia Power Inc.	New Waterford	NS	0.000	0.000	56,300	56,300
0444	Inco Limited	Copper Cliff	ON	52,906	0.000	0.000	52,906
5491	Stables Canada inc. Centre de traitement de résidus industriels	Blainville	QC	0.000	0.000	29,200	29,200
3414	Hudson Bay Mining and Smelting Company Ltd.	Flin Flon	MB	23,169	0.102	0.000	23,271
1708	New Brunswick Power	New Castle Creek	NB	0.065	1,591	19,624	21,280
2537	Safety-Kleen Ltd.	Corunna	ON	0.000	0.000	15,100	15,100
1861	Ontario Power Generation Inc	Nanticoke	ON	0.841	0.035	13,118	13,994
1809	Ontario Power Generation Inc	Courtright	ON	0.032	0.005	13,102	13,139
3385	Noranda Inc.	Murdochville	QC	11,300	0.533	0.000	11,833
1036	Sheerness Generating Station	Hanna	AB	0.000	0.000	9,627	9,627
2284	Trans-Alta Corporation	Duffield	AB	0.134	0.001	8,004	8,139
1473	Inco Limited	Thompson	MB	4,310	0.450	0.000	4,760
3197	Williams Operating Corporation	Marathon	ON	4,063	0.004	0.000	4,067
1467	Inco Limited	Walden	ON	3,938	0.000	0.000	3,938
1469	Inco Limited	Copper Cliff	ON	2,540	0.000	0.000	2,540
3802	Teck Cominco Metals Limited	Trail	BC	1,220	0.530	0.000	1,750
2710	Goldcorp Inc.	Balmertown	ON	0.069	1,511	0.000	1,580
2815	Falconbridge Ltd-Kidd Metallurgical Div.	Timmins/District of Cochrane	ON	1,361	0.104	0.000	1,465
0464	Jan Woodlands (2001) Inc.	Bancroft	ON	0.000	0.000	1,431	1,431
1471	Inco Limited	Port Colborne	ON	0.000	0.251	0.493	0.744
4024	Noranda Inc.	Belledune	NB	0.590	0.061	0.000	0.651
5153	Lafarge Canada Inc.	Kamloops	BC	0.501	0.000	0.000	0.501
5907	Northern Wood Preservers	Thunder Bay	ON	0.000	0.000	0.424	0.424
1236	Falconbridge Limited	Falconbridge	ON	0.264	0.006	0.000	0.270
3916	Noranda inc.	Montreal-Est	QC	0.219	0.000	0.000	0.219

Table 3 Emissions of Arsenic and its Compounds According to NPRI, 2002 (in tonnes) (continued)

NPRI ID	Company	City	Province	Emissions of Arsenic and Its Compounds (tonnes)			
				Air	Water	Land	Underground Total
4723	Vancouver Wharves Limited Partnership	North Vancouver	BC	0.166	0.009	0.038	0.000
1935	Placer Dome (CLA) Limited	Balmerston	ON	0.000	0.000	0.000	0.000
1465	Inco Limited	Copper Cliff	ON	0.000	0.118	0.000	0.000
5219	1126774 Ontario Ltd.	Snow Lake	MB	0.000	0.085	0.000	0.000
1698	New Brunswick Power	Belledune	NB	0.084	0.000	0.000	0.000
1484	Groupe Cambium	Sorel-Tracy	QC	0.000	0.000	0.000	0.000
0108	Barrick Gold Corporation	Kirkland Lake	ON	0.026	0.038	0.000	0.000
5655	Honeywell ASCa Inc.	Amherstburg	ON	0.000	0.035	0.000	0.000
6514	Envirofor Preservers (AB) Ltd.	Edmonton	AB	0.032	0.000	0.000	0.000
1568	Kinross Gold Corporation	Kirkland Lake	ON	0.000	0.025	0.000	0.000
5133	Paxton Forest Products Inc.	Monte Lake	BC	0.000	0.000	0.021	0.000
3158	Slater Stainless Corp.	Welland	ON	0.013	0.000	0.000	0.000
2161	Slater Steels Inc.	Hamilton	ON	0.011	0.000	0.000	0.000
1400	Newmont Canada Limited	Marathon	ON	0.006	0.002	0.000	0.000
1547	Metal Technologies-Woodstock Ltd.	Woodstock	ON	0.005	0.000	0.000	0.000
5166	North American Wood Treating	Abbotsford	BC	0.000	0.004	0.000	0.000
1508	Echo Bay Mines Ltd.	Contwoyto Lake	NU	0.000	0.003	0.000	0.000
5400	Ressources Breakwater	Clericy	QC	0.000	0.003	0.000	0.000
5185	J.R. Blackmore & Sons Ltd.	Cranbrook	BC	0.002	0.000	0.000	0.000
1785	NOVA Chemicals (Canada) Ltd.	Samia	ON	0.000	0.000	0.000	0.000
7072	Energy Plus 2000 Limited	Ajax	ON	0.000	0.000	0.000	0.000
2517	Spray Lake Sawmills (1980) Ltd.	Cochrane	AB	0.000	0.000	0.000	0.000
7096	Archie McCoy Hamilton Ltd	Troy	ON	0.000	0.000	0.000	0.000
2938	Zinc électrolytique du Canada Ltée	Valleyfield	QC	0.000	0.001	0.000	0.000

and the power and electrical utilities sector. In Alberta, the power and electrical utilities sector as well as the wood industry (wood preserving) contribute to arsenic emissions.

2.2.3 Ambient Levels

Ambient levels of arsenic are summarized in IPCS (2001). Mean arsenic levels in remote and rural areas range from 0.02 to 4 ng/m³. In urban areas, arsenic levels can range from 3 to 200 ng/m³. Values may be much higher in the vicinity of industrial sources (IPCS, 2001). Arsenic exists in ambient air in the form of arsenites and arsenates (IPCS, 2001).

Ambient air data in central Edmonton and central Calgary are available for the period June 1991 to November 2000 (AENV, 2003). Median and maximum arsenic concentrations associated with PM_{2.5} in ambient air were <0.1 and 3 ng/m³ (central Edmonton) and <0.1 to 5.9 ng/m³ (central Calgary) (AENV, 2003).

3.0 ATMOSPHERIC CHEMISTRY AND FATE

Most arsenic released into the atmosphere is associated with fine particles ($<2\ \mu\text{m}$) (Maggs, 2000; Coles *et al.* cited in IPCS, 2001), usually in the form of arsenate (+5 valence) and arsenite (+3 valence). The processes governing the fate of arsenic in the atmosphere are the same processes that govern the transport of these small particles. These processes include wet and dry deposition (ATSDR, 2000; CEPA, 1993). The average residence time has been estimated to be approximately 7 to 9 days (US EPA, 1984, Pacyna cited in ATSDR, 2000; Walsh *et al.* cited in CEPA, 1993). The residence time depends on particle size, meteorological conditions (Maggs, 2000; US EPA 1982 cited in IPCS, 2001) and conditions at the industrial source (stack exit velocity, stack height, etc.) (Maggs, 2000). As a result, particles containing arsenic can potentially travel thousands of kilometres (US EPA cited in ATSDR 2000; Pacyna cited in ATSDR, 2000).

4.0 EFFECTS ON HUMANS AND ANIMALS

Arsenic can exist in several different valence states as well as inorganic and organic compounds. Inorganic compounds appear to be more toxic than organic. There are many different forms of inorganic arsenic compounds; the most common naturally occurring forms are trivalent and pentavalent. The most common inorganic compounds are: arsenic trioxide (As_2O_3 , more common in air as dust), arsenates (AsO_4^{3-}) and arsenites (AsO_2^-) (both more common in water, soil, or food) (Goyer, 1996; ATSDR, 2000). Table 4 lists the common inorganic trivalent and pentavalent forms of As.

Table 4 Common Inorganic Arsenic Compounds^a

Valency	Compounds
Trivalent	Arsenic Trioxide
	Sodium Arsenite
	Arsenic Trichloride
Pentavalent	Arsenic Pentoxide
	Arsenic Acid
	Arsenates (lead arsenate, calcium arsenate)

^aGoyer, 1996.

Inorganic arsenic compounds are generally more toxic than organic forms, and the inorganic trivalent arsenites tend to be the more toxic of the inorganics (Gains, Byron *et al.*, Sardana *et al.*, Willhite, Maitani *et al.* cited in ATSDR, 2000); however, due to uncertainty in the data, the small differences in toxicity reported, and that many studies do not report the valence state of the As compound assessed, this report will assume that the level of toxicity for all the compounds is similar (as did ATSDR, 2000).

Humans appear to be substantially more sensitive to chronic arsenic toxicity than many laboratory animals (monkeys, dogs, rats) (Silver and Wainman, Byron *et al.*, Glazner *et al.*, Tay and Seah, Hindmarsh *et al.*, Heywood and Sortwell, Szuler *et al.*, Valentine *et al.*, Huang *et al.*, Guha Mazumder *et al.*, Barton *et al.*, Goddard *et al.*, Sass *et al.*, Prasad and Rossi, Haupt *et al.* cited in ATSDR, 2000). In addition, although animal studies of arsenic carcinogenicity are negative, arsenic has been demonstrated to produce cancer in humans (Goyer, 1996; ATSDR, 2000). This is important to consider as it negates the use of experimental animal toxicity studies as a good indicator of potential human toxicity (ATSDR, 2000).

The focus of this assessment was the adverse health effects associated with inhalation of inorganic arsenic compounds; oral and dermal effects were not reviewed in detail. The primary literature sources for this assessment were the Agency for Toxic Substances and Disease Registry (ATSDR, 2000) and the World Health Organization (WHO) (IPCS, 2001).

4.1 Overview of Chemical Disposition

Absorption of airborne inorganic As is dependant on the chemical form and on particle size. Both tri and pentavalent inorganic arsenics are well absorbed via inhalation; the more soluble

forms are more available than the less soluble forms. It appears, that nearly all the As deposited in the lungs is absorbed (Holland *et al.*, Pinto *et al.*, Vahter *et al.*, Offergelt *et al.* cited in ATSDR, 2000). Clearance from the lung is rapid and high (60-90% within 1 day) depending on the solubility of the compounds, the more soluble being absorbed faster (Rhoads and Sanders, Marafante and Vahter cited in ATSDR, 2000). Inorganic As is also very available via ingestion; some inhaled particles are cleared by the lungs and are available via the gastrointestinal tract. Dermal absorption is much lower (ATSDR, 2000).

After absorption, arsenites (trivalent As) are partially oxidized to arsenates (pentavalent As) and arsenates are partially reduced to arsenites resulting in a mixture of As(+3) and As(+5) available for circulation in the blood and metabolism (ATSDR, 2000). In addition, arsenites are methylated primarily in the liver, but also in other tissues (ATSDR, 2000). No studies of As distribution were identified for humans or animals after exposure via inhalation (ATSDR, 2000). Intratracheal instillation studies (simulates inhalation) reported As to be distributed throughout the body (liver, kidney, skeleton, gastrointestinal tract, and other tissues) (Rhoads and Sanders, 1985). Similar distribution occurred after oral and parenteral routes of exposure (ATSDR, 2000). Human and animal oral distribution studies indicate that As crosses through the placenta and into breast milk (Lugo *et al.*, Somogyi and Beck, Grandjean *et al.* cited in ATSDR, 2000). Distribution in rats is very different from human and other animal species (Lanz *et al.* cited in ATSDR, 2000).

In Humans, and some experimental animals (mice, hamsters, rabbits) the majority of the tri and pentavalent As as well as the methylated As compounds are excreted in the urine with a smaller amount excreted in the faeces. Some As remains bound to tissues (Crecelius, Smith *et al.*, Tam *et al.*, Vahter, 1981, 1986, Vahter and Envall, Vahter and Marafante, Lovell and Farmer, Maiorino and Aposhian, Marafante and Vahter, Hirata *et al.*, Takahashi *et al.*, Concha *et al.*, 1998a, 1998b, Kurtio *et al.* cited in ATSDR, 2000).

The exact mechanism of the genotoxicity of inorganic As compounds has not been established; however, two main mechanisms have been proposed: oxygen radical damage and impaired DNA repair process (IPCS, 2001).

4.2 Genotoxicity

Inhaled inorganic As is clastogenic in humans (Beckman *et al.*, Nordenson *et al.*, 1978a cited in ATSDR, 2000) and animals (Nagymajtenyi *et al.* cited in ATSDR, 2000). The animal study found increased chromosomal aberrations in the livers of fetuses from pregnant mice exposed to 22, but not 2.2 or 0.20, mg As/m³ as arsenic trioxide on days 9 to 12 of gestation (Nagymajtenyi *et al.* cited in ATSDR, 2000).

Inorganic As produced a number of clastogenic changes (sister chromatid exchanges, chromosomal aberrations, and DNA-protein cross-links) in human in vitro cell studies (Larramendy *et al.*, Okui and Fujiwara, Jha *et al.*, Wiencke and Yager, Dong and Luo, Rasmussen and Menzel cited in IPCS, 2001).

Inorganic As produced chromosomal aberrations in vitro in some animal cell studies (Larramendy *et al.*, Lee *et al.*, Kochhar *et al.*, Hei *et al.* cited in IPCS, 2001). Arsenic was not

genotoxic in some studies (Rossman et al., Lee et al. cited in IPCS, 2001), and weakly genotoxic in others (Oberly et al., Moore et al. cited in IPCS, 2001).

Inorganic As is not considered to be a direct acting genotoxin (IPCS, 2001).

4.3 Acute Effects

4.3.1 Acute Human Effects

Acute effects usually occur rapidly as a result of short-term exposures to high concentrations, and are of short duration – generally for exposures less than 24 hours (after Gallo, 1996). The majority of human inhalation exposure data available has been collected after occupational exposures. There are a number of limitations to be considered when using data from people exposed in the work place: i) the person exposed is generally a healthy, young to middle aged, male adult; ii) concurrent exposures to other chemicals are very likely; and, iii) the exposure concentrations are often difficult to define.

No deaths after acute As exposure have been reported via inhalation. Whereas, ingestion of large doses of As is reported to produce gastrointestinal problems, multi-organ failure, and death. Most of these symptoms have not been associated with acute inhalation of inorganic As (ATSDR 2000; IPCS, 2001).

Arsenic dusts are reported cause irritation of the respiratory system (mucus membranes in throat and nose), which can lead to laryngitis, bronchitis, or rhinitis (Dunlap, Pinto and McGill, Lundgren, Morton and Caron cited in ATSDR, 2000 and IPCS, 2001).

Gastrointestinal effects reported in workers exposed acutely via inhalation included: nausea, vomiting, and diarrhea (Pinto and McGill, Beckett *et al.*, Bolla-Wilson and Bleecker, Ide and Bullough, Morton and Caron cited in ATSDR, 2000 and IPCS, 2001). Because gastrointestinal effects are common with oral As exposure, these effects may be attributed to ingestion of As particles cleared from the lungs (ATSDR, 2000). Examples of exposure concentrations associated with these types of health effects are described further below and in Tables 5 and 6.

4.3.2 Acute and Sub-Acute Animal Effects

Sub-acute effects usually occur as a result of exposures to moderately high concentrations and are of an intermediate duration – generally for exposures lasting a few days to about 21 days. Table 5 lists some examples of the lowest and highest NOAELs (No Observable Adverse Effect Level) and LOAELs (Lowest Observable Adverse Effect Level) reported in the literature from acute animal studies. Table 6 lists some examples of the lowest and highest NOAELs (No Observable Adverse Effect Level) and LOAELs (Lowest Observable Adverse Effect Level) reported in the literature from sub-acute animal studies.

Below is a summary of potential effects associated with acute and sub-acute As inhalation. Details regarding exposure concentrations, duration of exposure and animal species examined are included in Tables 5 and 6.

4.3.2.1 Respiratory Effects

Sub-acute exposure to As dust produced severe respiratory problems in pregnant rats (laboured breathing and gasping) (Holson *et al.* cited in ATSDR, 2000). Intratracheal instillation in rats and hamsters produced irritation and hyperplasia in the lungs (Webb *et al.*, 1986, 1987, Goering *et al.*, Ohyama *et al.* cited in ATSDR, 2000). These respiratory effects may be due to exposure to particulates, not necessarily due to As toxicity (ATSDR, 2000).

Table 5 Examples of NOAELs and LOAELs Associated with Acute Arsenic Inhalation (Experimental Animals)

Effects Reported ^a	Exposure Period	Air Concentration (mgAs/m ³)	Species	Reference
Immunological/Lymphoreticular:				
Decreased pulmonary bactericidal activity; increased susceptibility to streptococcal infection. Less serious LOAEL.	3 hr	0.123 (trivalent)	Female mice.	ARNYI <i>ET AL.</i> CITED IN ATSDR, 2000.
Decreased pulmonary bactericidal activity; increased susceptibility to streptococcal infection. Less serious LOAEL.	5 d, 3 hr/d	0.519 (trivalent)	Female mice.	ARNYI <i>ET AL.</i> CITED IN ATSDR, 2000.
Developmental:				
NOAEL.	Gd ^b 9-12 4 hr/d	0.20 (trivalent)	Mice	Nagymajtenyi <i>et al.</i> cited in ATSDR, 2000.
Decreased average fetal body weight. Less serious LOAEL.	Gd ^b 9-12 4 hr/d	2.2 (trivalent)	Mice	Nagymajtenyi <i>et al.</i> cited in ATSDR, 2000.
Increased fetal deaths, skeletal malformations, and retarded growth. Less serious LOAEL.	Gd ^b 9-12 4 hr/d	(21.6) (trivalent)	Mice	Nagymajtenyi <i>et al.</i> cited in ATSDR, 2000.

^a NOAEL, Less serious LOAEL, and Serious LOAEL as identified by (ATSDR, 2000).

^b Gd – gestational days.

Table 6 Examples of NOAELs and LOAELs Associated with Sub-Acute Arsenic Inhalation (Experimental Animals)

Effects Reported ^a	Exposure Period	Air Concentration (mgAs/m ³)	Species	Reference
Death:	14 d premating thru Gd ^b 19. 7 d/wk, 6 hr/d	20 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.
Systemic:				Holson <i>et al.</i> cited in ATSDR, 2000.
Respiratory system. NOAEL.	14 d premating thru Gd ^b 19. 7 d/wk, 6 hr/d	2 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.
Respiratory system: rales, dried material around nose. Less serious LOAEL	14 d premating thru Gd ^b 19. 7 d/wk, 6 hr/d	8 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.
Respiratory system: laboured breathing, gasping. Serious LOAEL.	14 d premating thru Gd ^b 19. 7 d/wk, 6 hr/d	20 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.
Body weight. NOAEL.	14 d premating thru Gd ^b 19. 7 d/wk, 6 hr/d	8 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.
Decreased body weight gain during gestation. Less serious LOAEL	14 d premating thru Gd ^b 19. 7 d/wk, 6 hr/d	8 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.
Drastic decrease in body weight. Serious LOAEL.	14 d premating thru Gd ^b 19. 7 d/wk, 6 hr/d	20 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.
Gastrointestinal: NOAEL	14 d premating thru Gd ^b 19. 7 d/wk, 6 hr/d	8 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.
Gastrointestinal lesions. Serious LOAEL	14 d premating thru Gd ^b 19. 7 d/wk, 6 hr/d	20 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.

Table 6 Examples of NOAELs and LOAELs Associated with Sub-Acute Arsenic Inhalation (Experimental Animals) (continued)

Effects Reported ^a	Exposure Period	Air Concentration (mgAs/m ³)	Species	Reference
Immunological/Lymphoreticular:				
NOAEL.	4 wk, 5 d/wk, 3 hr/d	0.126 (trioxide)	Female mice.	Arnyi <i>et al.</i> cited in ATSDR, 2000.
Decreased pulmonary bactericidal activity. Less serious LOAEL.	4 wk, 5 d/wk, 3 hr/d	0.245 (trioxide)	Female mice.	Arnyi <i>et al.</i> cited in ATSDR, 2000.
Reproductive Effects:				
NOAEL.	14 d pre-mating thru Gd ^b 19. 7 d/wk, 6 hr/d	8 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.
Marked increase in post-implantation loss and in viable fetuses. Less serious LOAEL.	14 d pre-mating thru Gd ^b 19. 7 d/wk, 6 hr/d	20 (trioxide)	Female rats.	Holson <i>et al.</i> cited in ATSDR, 2000.

^a NOAEL, Less serious LOAEL, and Serious LOAEL as identified by (ATSDR, 2000).

^b Gd – gestational days.

4.3.2.2 Developmental Effects

Serious developmental effects have been reported to occur in mice and rats after inhalation of As during gestation (Nagymajtenyi *et al.*, Holson *et al.* cited in ATSDR, 2000). It could not be determined whether the developmental effects were due to As poisoning or maternal toxicity (ATSDR, 2000).

4.3.2.3 Carcinogenic Effects

Three As inorganic compounds were administered via intratracheal instillation (simulates inhalation) to examine the carcinogenic potential of As in hamsters (Ishinishi *et al.*, Pershagen *et al.*, Pershagen and Bjorklung, Yamamoto *et al.* cited in IPCS, 2001). The results were inconclusive and did not reflect the carcinogenic potential demonstrated in human inhalation exposure studies (IPCS, 2001).

4.3.2.4 Other Effects

Many studies describe gastrointestinal effects of arsenic poisoning after oral exposures, however, only one animal study was identified which described gastrointestinal effects after sub-acute exposures via inhalation (Holson *et al.* cited in ATSDR, 2000). This same study also reported reduced body weight gain and food consumption in pregnant rats.

Animals exposed via inhalation and intratracheal instillation were reported to have an increased susceptibility to respiratory pathogens, indicating a potential immune system effect (Aranyi *et al.*, Sikorski *et al.*, Burns and Munson cited in ATSDR, 2000).

4.4 Chronic Effects

4.4.1 Chronic Human Effects

Chronic effects generally occur as a result of long-term exposure to low concentrations, and are of long duration – generally as repeated exposures for more than 12 months (Gallo, 1996). The majority of human inhalation exposure data available has been collected after occupational exposures. There are a number of limitations to be considered when using data from people exposed in the work place; i) the person exposed generally is a healthy, young to middle aged, male adult; ii) concurrent exposures to other chemicals are very likely; and, iii) the exposure concentrations are often difficult to define.

Table 7 lists some examples of the lowest and highest NOAELs (No Observable Adverse Effect Level) and LOAELs (Lowest Observable Adverse Effect Level) reported in the literature.

Below is a summary of potential effects associated with chronic As inhalation. Details regarding exposure concentrations and durations of exposure are included in Table 7.

4.4.1.1 Respiratory Effects

Arsenic is a known irritant, however, very few investigations into the effects of inhaled As dust have been documented in humans (ATSDR, 2000). Effects typical of particulate inhalation have been reported (irritation of mucus membranes, laryngitis, bronchitis, rhinitis) (Dunlap, Pinto and McGill, Lundgren cited in ATSDR, 2000; Morton and Caron cited in ATSDR, 2000 and IPCS, 2001) and extremely high exposure can result in perforation of the nasal septum (Dunlap, Pinto and McGill, Sandstrom *et al.* cited in ATSDR, 2000). Perry *et al.* (cited in ATSDR, 2000) reported no differences in chest x-rays and respiratory tests of exposed men (sodium arsenite) from unexposed men. However, reports of increased mortality due to non-malignant lung diseases (e.g., emphysema, pneumonia) have been published for men exposed occupationally (Lee-Feldstein, 1983a, 1983b cited in ATSDR, 2000; Welch *et al.* cited in ATSDR, 2000 and IPCS, 2001; Xuan *et al.* cited in ATSDR, 2000; Enterline *et al.* cited in ATSDR, 2000 and IPCS, 2001). However, due to confounding factors in these studies, an association between inhaled As and respiratory effects could not be made (ATSDR, 2000).

4.4.1.2 Vascular and Cardiovascular Effects

Ingestion of As has been well characterized to produce adverse vascular and cardiovascular effects (ATSDR, 2000; IPCS, 2001). Inhalation also appears to adversely affect the vascular system producing: increased incidence of Raynaud's phenomenon (peripheral vascular disease), vasospasticity (constriction of the blood vessels resulting in cold hands and feet, white fingers, and numb fingers and feet); decreased systolic blood pressure (Lagerkvist *et al.*, Jensen and Hansen cited in ATSDR, 2000). These effects tended to diminish once exposure decreased (Lagerkvist *et al.* cited in ATSDR, 2000 and IPCS, 2001).

Table 7 Examples of NOAELs and LOAELs Associated with Chronic Arsenic Inhalation (Human)

Effects Reported ^a	Exposure Period	Air Concentration (mgAs/m ³)	Reference
Systemic:			
Cardiovascular: Increased incidence of vasospasticity and clinical Raynaud's phenomenon. Serious LOAEL.	23 yr (average)	0.36 (trioxide)	Lagerkvist <i>et al.</i> cited in ATSDR, 2000.
Dermal: mild pigmentation of the skin. Less serious LOAEL	0.5-50 yr	0.078 (trioxide)	Perry <i>et al.</i> cited in ATSDR, 2000.
Dermal: gross pigmentation with hyperkeratinization of exposed areas, wart formation. Serious LOAEL.	0.5-50 yr	0.613 (trioxide)	Perry <i>et al.</i> cited in ATSDR, 2000.
Dermal: dermatitis. Less serious LOAEL.	6-8 yr, 8 hr/d	0.007 (trioxide)	Mohamad cited in ATSDR, 2000.
Respiratory: NOAEL.	0.5-50 yr	0.613 (trioxide)	Perry <i>et al.</i> cited in ATSDR, 2000.
Neurological Effects:			
Decreased nerve conduction velocity. Less serious LOAEL.	28 yr (Average)	0.31 (trioxide)	Lagerkvist and Zetterlund cited in ATSDR, 2000
Developmental:			
NOAEL.	Living near an As pesticide factory.	0.00005 (trioxide)	Ihrig <i>et al.</i> cited in ATSDR, 2000.
Increased risk for stillbirth. Less serious LOAEL.	Living near an As pesticide factory.	0.0007 (trioxide)	Ihrig <i>et al.</i> cited in ATSDR, 2000.

Table 7 Examples of NOAELs and LOAELs Associated with Chronic Arsenic Inhalation (Human) (continued)

Effects Reported ^a	Exposure Period	Air Concentration (mgAs/m ³)	Reference
Cancer:			
Lung Cancer. Serious LOAEL.	1->30 yr	0.213 (trioxide)	Enterline <i>et al.</i> , 1987a cited in ATSDR, 2000.
Lung Cancer. Serious LOAEL.	19.3 yr (average)	0.069 (trioxide)	Enterline <i>et al.</i> , 1987b cited in ATSDR, 2000.
Lung Cancer. Serious LOAEL.	3 mo->30 yr	0.2 (trioxide)	Jarup and Pershagen cited in ATSDR, 2000.
Lung Cancer. Serious LOAEL.	3 mo->30 yr	0.05 (trioxide)	Jarup <i>et al.</i> cited in ATSDR, 2000.
Lung Cancer. Serious LOAEL.	1->30 yr	0.38 (trioxide)	Lee-Feldstein cited in ATSDR, 2000.
Lung Cancer. Serious LOAEL.	14 yr (average)	0.3 (trioxide)	Welch <i>et al.</i> cited in ATSDR, 2000.

^a NOAEL, Less serious LOAEL, and Serious LOAEL as identified by (ATSDR, 2000).

Some cohort studies reported an increase in mortality from cardiovascular disease in men exposed to As in the workplace; however, an association between As exposure and cardiac effects could not be conclusively made (Axelson *et al.* cited in ATSDR, 2000 and IPCS, 2001; Wall cited in ATSDR, 2000; Welch *et al.* cited in ATSDR, 2000 and IPCS, 2001; Lee-Feldstein, 1983b cited in ATSDR, 2000; Jarup *et al.*, Enterline *et al.* cited in ATSDR, 2000 and IPCS, 2001; Tollestrup *et al.*, Xuan *et al.* cited in ATSDR, 2000; Qiao *et al.* cited in ATSDR, 2000 and IPCS, 2001; Lubin *et al.*, Lubin and Fraumeni cited in IPCS, 2001). Other studies reported no adverse cardiovascular effects (Tokudome and Kuratsune, Armstrong *et al.* cited in IPCS, 2001; Sobel *et al.*, Jarup *et al.* cited in ATSDR, 2000 and IPCS, 2001).

4.4.1.3 Neurological Effects

Adverse neurological effects have been reported in workers exposed to As via inhalation (Feldman *et al.* cited in ATSDR, 2000 and IPCS, 2001; Blom *et al.* cited in ATSDR, 2000; Beckett *et al.*, Bolla-Wilson and Bleecker cited in ATSDR, 2000 and IPCS, 2001; Ide and Bullough cited in ATSDR, 2000; Morton and Caron cited in ATSDR, 2000 and IPCS, 2001; Lagerkvist and Zetterlund, 1994). The effects reported included: peripheral neuropathy

(numbness, loss of reflexes, muscle weakness, tremors), frank encephalopathy (hallucinations, agitation, emotional lability, memory loss).

Peripheral neuropathy and encephalopathy are also common with ingestion of As (ATSDR, 2000; IPCS, 2001).

4.4.1.4 Developmental Effects

There is some evidence that inhalation of As may result in an increase of maternal toxemia, spontaneous abortion and stillbirths, an increase in congenital malformations, and decreased average birth weight in families whose mothers worked in a local smelter and families living in the vicinity of an arsenic source (Nordstrom *et al.*, 1978a, 1978b cited in ATSDR, 2000 and IPCS, 2001; Nordstrom *et al.*, 1979a, 1979b cited in ATSDR, 2000; Tabacova *et al.*, 1994a, 1994b cited in IPCS, 2001; Ihrig *et al.* cited in ATSDR, 2000). However, confounding factors in these studies made it difficult to conclusively attribute these effects to inhalation of As (ATSDR, 2000).

4.4.1.5 Carcinogenic Effects

Inhalation of inorganic As increases the risk of lung cancer in humans. Most of the studies examine workplace exposures (smelters, mines, chemical plants), however, inorganic As is considered to be the causative agent. The risk of lung cancer increases with increased As exposure (after ATSDR, 2000 and IPCS, 2001). Tobacco smoking may interact with As and further increase risk of lung cancer (ATSDR, 2000; IPCS (2001).

Small increases in lung cancer have been reported in people living near industrial sources of inorganic As (Matanoski *et al.*, Cordier *et al.*, Brown *et al.*, Pershagen cited in ATSDR, 2000; Lubin *et al.* cited in IPCS, 2001). Some studies of communities in the vicinity of smelters report an increased risk of lung cancer among men, but not women (Xu *et al.* cited in IPCS, 2001), others did not detect a statistical difference (Marsh *et al.*, 1997, 1998 cited in IPCS, 2001). Hughes *et al.* (cited in IPCS, 2001) notes the risk of lung cancer in may be too low to identify by the statistical analysis.

Other non-respiratory cancers (large intestine, bone, stomach, colon, childhood cancers, sinonasal, hepatic, kidney, skin) have been reported to possible be due to inhalation of inorganic As; however, the data are not conclusive (Lee and Fraumeni, Welch *et al.*, Lee-Feldstein, 1983a, 1986 cited in ATSDR, 2000 and IPCS, 2001; Sandström *et al.*, Wong *et al.*, Wingren and Axelson cited in ATSDR, 2000; Simonato *et al.* cited in IPCS, 2001; Enterline *et al.* cited in ATSDR, 2000 and IPCS, 2001; Battista *et al.* cited in ATSDR, 2000; Bulbulyan *et al.* cited in ATSDR, 2000 and IPCS, 2001; Wulff *et al.*, Tsai *et al.* Tsuruta *et al.*, Çöl *et al.* cited in ATSDR, 2000). Some studies found no statistical increase in some non-respiratory cancers (Tokudome and Kuratsune cited in IPCS, 2001; Wong *et al.* cited in ATSDR, 2000; Simonato *et al.*, Lubin *et al.* cited in IPCS, 2001).

Ingestion of As increases risk of skin, kidney, and bladder cancers (IPCS, 2001).

4.4.1.6 Other Effects

Many studies report As inhalation to produce severe dermatitis (hyperpigmentation, folliculitis, multiple warts, superficial ulcerations) in workers (Dunlap, Pinto and McGill, Lagerkvist *et al.*, Mohamed cited in ATSDR, 2000). Dermal effects are very common after ingestion of inorganic As (ATSDR, 2000). Dunlap and Pinto and McGill (cited in ATSDR, 2000) reported chemical conjunctivitis (redness, swelling, and pain of the eyes) in workers usually demonstrating dermal effects also. A few occupational studies report a potential increase in risk of diabetes in workers exposed to As (Rahman and Axelson Rahman *et al.* cited in IPCS, 2001; Jensen and Hansen cited in ATSDR, 2000 and IPCS, 2001).

4.4.2 Chronic Animal Effects

No recent long-term inhalation studies in animals were identified (ATSDR, 2000; IPCS, 2001).

Chronic ingestion studies indicate that animals are not as sensitive as humans to the chronic effects of inorganic As. The majority of experimental animal studies have not reported cancer in association with As ingestion. ATSDR (2000) and IPCS (2001) report that most of the animal studies published have a number of limitations (high doses (total doses ranging from 0.1-200 mg As), limited exposure time, limited animal numbers), which makes experimental animal models bad indicators of human toxicity (ATSDR, 2000; IPCS, 2001). A single preliminary ingestion study of low dose sodium arsenate (2-2.5 µg As/day) reported treatment-related tumour in mice (Ng *et al.*, cited in IPCS, 2001).

4.5 Summary of Adverse Health Effects of Arsenic Inhalation

Acute human exposure to arsenic dusts can cause irritation of the respiratory system (mucus membranes in throat and nose), which can lead to laryngitis, bronchitis, or rhinitis. Sub-acute animal exposures produced severe respiratory problems possibly due to exposure to particulates, not necessarily due to As toxicity. Sub-acute exposures in animals were reported to increase susceptibility to respiratory pathogens, indicating a potential immune system effect.

Chronic human exposures have been reported to: result in irritation of the respiratory tract, have cardiovascular and neurological effects, produce severe dermatitis, and increase the risk of lung cancer. Other non-respiratory cancers (large intestine, bone, stomach, colon, childhood cancers, sinonasal, hepatic, kidney, skin) have been reported to possibly be due to inhalation of inorganic As; however, the data is not conclusive. Chronic ingestion of As increases risk of skin, kidney, and bladder cancers.

Humans appear to be substantially more sensitive to chronic As toxicity than many laboratory animals. Carcinogenicity has not been demonstrated in animal studies. This is important to consider as it negates the use of experimental animal toxicity studies as a good indicator of potential human toxicity.

5.0 EFFECTS ON MATERIALS

Most of the metals emitted to the atmosphere are associated with particulate matter at ambient temperatures or – less frequently – in the vapor state. Metal oxides tend to be adsorbed to or associated with particles. This is the case for numerous individual metals (after WBK, 2003):

- Arsenic occurs naturally in soil and minerals and may enter the air as wind-blown dust particles. Arsenic released from combustion processes is usually attached to very small particles.
- Cobalt is probably emitted in the particulate form to the air, since compounds of cobalt are not usually volatile.
- Copper is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter.
- Elemental manganese and inorganic manganese compounds have negligible vapor pressures but may exist in air as suspended particulate matter derived from industrial emissions or the erosion of soils.
- Nickel releases to the atmosphere are mainly in the form of aerosols that cover a broad spectrum of sizes. Nickel, from power plants and smelters, tends to be associated with small particles.
- Vanadium generally enters the atmosphere as an aerosol. Vanadium attributed to combustion of residual fuel oils and coal is generally in the form of vanadium oxides and contributes to approximately two-thirds of the atmospheric vanadium.
- Zinc occurs in the environment mainly in the divalent (+2) oxidation state. It is found in the atmosphere at the highest concentrations in small particles.

Thus the predominant issue with respect to ambient emissions of metals negatively affecting material surfaces will be because of its association with deposited airborne particulate matter. Excluding acidic particles, deposition of airborne particles on material surfaces can cause soiling (Baedecker *et al.*, 1991). In addition, particles deposited on a surface can adsorb or absorb acidic gases (e.g. SO₂ and NO₂), thus serving as nucleation sites for these acidic gases. This may accelerate physical and chemical degradation of material surfaces that normally occur when materials are exposed to environmental factors such as wind, sun, temperature fluctuations, and moisture.

Haynie and Lemmons (1990) described soiling as the contrast in reflectance of particles on a substrate compared to the reflectance of a bare substrate. Soiling of materials is a concern because it results in more frequent cleaning and repainting, thereby reducing its lifetime usefulness and increasing costs associated with maintenance of the materials.

Haynie (1986) reported that it is difficult to determine the amount of deposited particles that cause an increase in soiling. However, Haynie (1986) indicated that soiling is dependent on the particle concentration in the ambient environment, particle size distribution, and the deposition rate and the horizontal or vertical orientation and texture of the surface being exposed. Schwar (1998) reported that the buildup of particles on a horizontal surface is counterbalanced by an equal and opposite depletion process. The depletion process is based on the scouring and washing effect of wind.

6.0 AIR SAMPLING AND ANALYTICAL METHODS

6.1 Introduction

Accurate measurement of trace metals in ambient air is often difficult, in part because of the variety of substances, the variety of potential techniques for sampling and analysis, and the lack of standardized and documented methods. The United States Environmental Protection Agency (US EPA, 1999a), National Institute of Occupational Safety and Health (NIOSH, 1994), and Occupational Safety and Health Administration (OSHA, 2002a; 2002b) are the only organizations that provide documented and technically reviewed methodologies for determining the concentrations of selected trace metals of frequent interest in ambient and indoor air. It is these methods, which are presented here, that are generally accepted as the preferred methods for trace metal sampling and analysis.

6.2 Sampling Methods

The majority of trace metals present in ambient air are particle-bound. Therefore, the sample collection schemes appropriate for the collection of trace metals follow the methods appropriate for particulate matter measurements. There are many sampling systems available for particulate matter measurements, each with its own advantages and disadvantages. Only some, however, are capable of collecting samples that are suitable for elemental analysis. The major prerequisites in selecting a sampling system are to determine what size range of particles are to be monitored, what trace metals are of interest, and the appropriate method of analysis. The analytical method selection is very important, because only some methods are compatible with each sampling system. The available documented and technically reviewed methods include high volume samplers for collecting TSP (total suspended particulate with aerodynamic diameters less than 100 μm) and PM_{10} (particulate matter with aerodynamic diameters less than 10 μm) and low volume samplers for collecting PM_{10} and $\text{PM}_{2.5}$ (particulate matter with aerodynamic diameters less than 2.5 μm) utilizing dichotomous and Partisol samplers. Each of these samplers has the ability to collect particulate matter uniformly across the surface of the filters and they are commonly used in Alberta. They can be used to determine average ambient particulate matter concentration over the sampling period, and the collected material can subsequently be analyzed for inorganic metals and other materials present in the collected sample. Some of the advantages and disadvantages associated with the sampling options are summarized in Table 8.

6.2.1 *Hi-Vol Sampler*

The primary method used to sample airborne particulate matter in a volume of ambient air with the objective of identifying and quantifying the inorganic metals present has historically been the high volume (hi-vol) sampler (US EPA, 1999a). Air is drawn into the sampler and through a glass fiber or quartz filter by means of a blower (typically at a rate of 1.13 to 1.70 m^3/min), so that particulate material collects on the filter surface. If a 10 μm size-selective inlet is used, only particles of 10- μm size and less enter the sampling inlet and are collected on the downstream filter. Without the inlet, particles of 100- μm size and less are collected. When glass fiber filters are used, particles 100 μm or less are ordinarily collected. With a size-select inlet, particles

10 μm or less are collected on quartz filters. The hi-vol's design causes the particulate matter to be deposited uniformly across the surface of the filter. The mass concentration of suspended particulates in the ambient air is computed by measuring the mass of collected particulates and the volume of air sampled. After the mass is measured, the filter is ready for extraction to determine the metal concentration.

Because of its higher flow rates, the hi-vol collects more material so lower ambient concentrations of inorganic materials can be detected (assuming identical filter medium and analysis technique). The major interferences in suspended particulate matter determination are collection of large extraneous objects (e.g., insects), collection of liquid aerosols and gas or vapours that may react with some filter types and/or collected materials to add artificial weight (ARPEL, 1998). The high-volume sampling technique has been recommended as the method for sampling ambient particulate matter by most air quality agencies including the US EPA and Environment Canada. As delineated later, airborne particulate matter retained on the filter may be examined or analyzed chemically by a variety of methods including inductively coupled plasma (ICP) spectroscopy, inductively coupled plasma/mass spectroscopy (ICP/MS), flame atomic absorption (FAA) spectroscopy, graphite furnace atomic absorption (GFAA) spectroscopy, and instrumental neutron activation analysis (INAA).

6.2.2 *Dichotomous Sampler*

Dichotomous samplers are used to sample airborne particulate matter in coarse (2.5 to 10 μm) and fine (<2.5 μm) size fractions. In dichotomous samplers, ambient air is drawn at a flow rate of approximately 1 m^3/hr . The coarse fraction of particulate matter is accelerated into the central collection filter while the fine fraction is drawn onto a second collection filter. Particles that are <10 μm are collected via a 10 μm inlet and separated into fine (<2.5 μm) and coarse (2.5 to 10 μm) fractions by a virtual impactor. In recent literature of ambient air particulate sampling and elemental analysis, the duration of sampling ranges from 12 to 24 hours depending upon experimental design and amount of ambient particulate present (US EPA, 1999). The mass concentration of airborne particles within each size range is determined gravimetrically. The detection limit for the method depends on the sensitivity of the analytical balance utilized for the gravimetric determination and the volume of air sampled. The dichotomous sampler has the advantage of collecting two fractions so that information can be obtained about total PM_{10} and/or both of the two fractions. In addition, the dichotomous sampler operates at a low flow rate, which allows the use of filter media that would otherwise quickly clog at high-volume flow rates. The particles are collected on Teflon filters and once at the laboratory are analyzed by X-ray fluorescence (XRF) spectrometry, proton induced X-ray emissions (PIXE) spectrometry, or instrumental neutron activation analysis (INAA).

6.2.3 *Partisol Sampler*

The Rupprecht and Patashnick (R&P) Low-Volume Partisol Air Sampler is a microprocessor-controlled manual sampler with a unique set of features that make it a suitable platform for measuring particulate and other constituents found in the atmosphere (US EPA, 1999a). Ambient air is drawn through a low flow (16.7 L/min) PM_{10} or $\text{PM}_{2.5}$ inlet where particle size selection takes place. The particulate-laden air is then directed through a collection filter composed of either quartz, Teflon-coated glass, or Teflon where the particulate matter is

collected. A mass flow control system maintains the sample flow through the system at the prescribed volumetric flow using information from sensors that measure the ambient temperature and ambient pressure. The sample filter is conditioned and weighed both before and after sample collection to determine the amount of mass collected during the sampling period. The airborne particulate collected on the 47-mm filter in the Partisol Sampler may be subjected to a number of post-collection chemical analytical techniques to ascertain the composition of the material caught by the filter. Appropriate techniques include X-ray fluorescence (XRF) spectrometry, proton induced X-ray emissions (PIXE) spectrometry, and instrumental neutron activation analysis (INAA). The type of filter media should be compatible with the analytical method used.

6.2.4 *Alternative Sampling Methods*

In addition to the documented and technically reviewed methodologies for collecting trace metals in ambient air there are alternative methods. One such method is the Portable Minivolume Air Sampler (MiniVol) made by Airmetrics (Airmetrics, 1998). The MiniVol works by drawing air through a size-selective impactor that removes the unwanted larger sizes of particulate and captures the smaller sizes on a filter. It has a twin cylinder vacuum pump that is designed to pull air at 5 L/min (at standard temperature and pressure) through an impactor that is capable of removing particles larger than the cut-points of either 10 μm or 2.5 μm . This active sampler is operated by the principle of inertial impaction using a single stage impactor with a filter. In this device, the particle-laden air is accelerated through one nozzle and the exiting jet impinges upon a plate. The impactor dimensions are chosen such that particles smaller than the desired cut-point follow the streamlines as they bend at the impaction plate, while the larger particles with sufficient inertia depart from the streamlines and impact against the plate. The elemental and morphological properties of the deposited material are later analyzed using an appropriate technique (Jones *et al.*, 1998; Tropp *et al.*, 1998). Environment Canada uses the MiniVol as a saturation sampler and they have been used extensively in several parts of Alberta under a variety of climatic conditions (Alberta Health, 1997).

6.3 *Analytical Methods*

Many analytical methods exist to characterize trace metals collected on a filter substrate and each has its own attributes, specificities, advantages and disadvantages. Though several methods are multi-species (able to quantify a number of different chemical components simultaneously) no single method is sufficient to quantify both the majority of the collected particulate matter mass and those trace elements which may be of interest. The type of analytical technique used is generally dictated by the specific sampling method employed to collect the particulate matter. Furthermore, the type of filter medium used to capture the sample is a factor in the choice of analytical technique and vice-versa. Most importantly, the choice of analytical method will depend on the metals of interest and the detection limits desired. Some of the advantages and disadvantages associated with the analytical options are summarized in Table 8. While factors such as element specificity and sensitivity are critically important, considerations such as cost and throughput (the number of samples and number of elements to be determined per sample) are also significant.

6.3.1 Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy (AAS) has occasionally been used as the primary method for metals determination (Becerro-Gonzalez *et al.*, 1997), but is more commonly used as a supplementary technique for elements not amenable to analysis by one of the multi-elemental techniques described later (Kowalczyk *et al.*, 1982; Rizzio *et al.*, 2000). In this method, trace metals in a particulate matter sample are extracted by either a hot acid or microwave extraction procedure into a solution and subsequently vaporized in a flame. A light beam with a wavelength matching the absorption wavelength of the metal of interest passes through the vaporized sample. The light attenuated by the sample is then measured and the amount of the metal present is determined using Beer's Law (Koutrakis and Sioutas, 1996).

AAS describes both flame atomic absorption (FAA) spectroscopy and graphite furnace atomic absorption (GFAA) spectroscopy (US EPA, 1999a). The two atomic absorption analyses options are similar in that the measurement principle is the same. However, they differ in how the sample is introduced into the instrument. Both types of atomic absorption spectroscopy involve irradiating the sample with light of a single wavelength and measuring how much of the input light is absorbed. Each element absorbs light at a characteristic wavelength and, therefore, analysis for each element requires a different light source. This means only one element can be determined at a time. In FAA, the sample is atomized and introduced into the optical beam using a flame, typically air/acetylene or nitrous oxide/acetylene. In GFAA, a graphite furnace electrothermal atomizer is used.

AAS has the advantage of being able to accurately measure difficult elements such as cadmium, lead, zinc and magnesium. However, the necessary dissolution of collected particulate and the manipulation of a solution of trace elements is not a trivial thing. Furthermore, AAS can only analyze one element at a time thus rendering the analysis of an extensive set of elements prohibitively time consuming. The analytical technique is also destructive and requires that the sample be extracted or digested for introduction into the system in solution. The detection limit of GFAA is typically about two orders of magnitude better than FAA (US EPA, 1999a). High-volume samplers are typically used for sampling when FAA or GFAA analysis is planned.

6.3.2 X-Ray Fluorescence Spectroscopy

In X-Ray Fluorescence (XRF) (Dzubay and Stevens, 1975; Dzubay, 1977; Lewis and Macias, 1980; Price *et al.*, 1982; Dzubay *et al.*, 1988; Glover *et al.*, 1991; Schmeling *et al.*, 1997) a beam of X-rays irradiates the particulate matter sample. This causes each element in the sample to emit characteristic X-rays that are detected by a solid-state detector or a crystal spectrometer. The characteristic X-ray is used to identify the element and the intensity is used to quantify the concentration of the measured element. X-ray fluorescence spectrometry (including energy dispersive and wavelength dispersive modes) can be accurately used for all elements with atomic weights from 11 (sodium) to 92 (uranium). Furthermore, multiple elements can be determined simultaneously.

This method has the advantages of being non-destructive, requiring minimal sample preparation, providing immediate results and having low equipment cost. However, the detection limit is higher than other analysis techniques. In addition, it requires a thin collection deposit (i.e. 10 to

50 $\mu\text{g}/\text{cm}^2$) and it involves complex matrix corrections. Elements lighter than aluminum are often difficult to determine because of their low fluorescent yields and particularly because of the strong absorption of fluorescent X-rays by the substrate on which they are collected (US EPA, 1999a). Because high-volume samplers utilize quartz-filters that cause high background when employing XRF, analysis by XRF usually requires Teflon or Nylon filters used in the dichotomous or the Partisol samplers.

6.3.3 *Inductively Coupled Plasma Spectroscopy*

In Inductively Coupled Plasma (ICP) Spectroscopy analysis, the particulate matter sample is excited using an argon plasma torch (ARPEL, 1998; US EPA, 1999a). When the excited atoms return to their normal state, each element emits a characteristic wavelength of light. The wavelengths detected and their intensities indicate the presence and amounts of particular elements. Samples containing up to 61 preselected elements can be simultaneously analyzed by ICP at a rate of one sample per minute (US EPA, 1999a). In addition, the ICP technique has the ability to analyze a large range of concentrations. As with FAA and GFAA, the particulate matter must be extracted (via hot acid extraction or microwave extraction) and digested for ICP analysis, and the material introduced into the instrument is destroyed during analysis. An ICP instrument is more costly than many of the other instruments. The ICP detection limit for many of the elements of interest is equal to or somewhat better than most of the other instruments. High-volume samplers are typically used for sampling when ICP analysis is planned.

6.3.4 *Inductively Coupled Plasma/Mass Spectroscopy*

Other analytical methods such as Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) can be used to determine trace metal concentrations (Broekaert *et al.*, 1982; Janssen *et al.*, 1997). In ICP/MS analysis, the sample is excited using an argon plasma torch to generate elemental ions for separation and identification by mass spectrometry. This analysis allows many more than sixty elements and the isotopes of elements to be determined simultaneously at very low detection limits. However, ICP/MS analysis is time consuming because the sample must be extracted or digested and the analysis is destructive. In addition, the procedure is very costly and its documented applications are the lowest among all the potential techniques (US EPA, 1999a). Sampling is typically conducted using high-volume samplers when ICP/MS analysis is planned.

6.3.5 *Proton Induced X-Ray Emission Spectroscopy*

Some work on trace metal analysis has also been performed using Proton Induced X-Ray Emission (PIXE) Spectroscopy (Heidam, 1981; Van Borm *et al.*, 1990; Flores *et al.*, 1999). PIXE analysis is very similar to XRF analysis in that the sample is irradiated by a high-energy source, in this case high-energy protons, to remove inner shell electrons. Fluorescent X-ray photons are detected employing the same detection methods as XRF and used to identify and quantify different elements in the sample.

PIXE is one of the more commonly used elemental analysis methods because of its relatively low cost, nondestructive, multi-element capabilities. It is potentially capable of determining 72 elements with molecular weights between those of sodium and uranium, simultaneously (ARPEL, 1998). The method provides the sensitivity for accurate measurements at the

nanogram or less level for many important trace metals in the urban atmosphere. The PIXE method has the ability to analyze a very small sample diameter in addition to evenly distributed wide-area samples, which is advantageous because it permits analysis of individual particle size fractions collected with single orifice type cascade impactors. PIXE is capable of measuring smaller quantities of particulate matter, although it has the same limitations as with XRF concerning light elements. In addition, facilities for this method are expensive and not common and it is less suitable for routine filter analysis than other multi-elemental methods because of more complicated sample preparation (US EPA, 1994). Analysis by PIXE typically involves collecting particulate matter by dichotomous or Partisol samplers.

6.3.6 Instrumental Neutron Activation Analysis Spectroscopy

Instrumental Neutron Activation Analysis (INAA) (Zoller and Gordon, 1970; Gladney *et al.*, 1974; Hopke *et al.*, 1976; Mizohata and Mamuro, 1979; Kowalczyk *et al.*, 1978, 1982; Olmez, 1989; Rizzio *et al.*, 1999; Salma and Zemplem-Papp, 1999) bombards a sample with a high neutron thermal flux in a nuclear reactor or accelerator. The sample elements are transformed into radioactive isotopes that emit gamma rays. The distribution or spectrum of energy of the gamma rays can be measured to determine the specific isotopes present. The intensity of the gamma rays can also be measured and is proportional to the amounts of elements present.

INAA is a simultaneous, multi-element method for determining ppt, ppm or ppb levels of 40-50 elements of interest. It has the advantage of higher sensitivity compared to other methods, a fact that makes it attractive for sampling trace elements found in extremely low concentrations (US EPA, 1999a). INAA is a non-destructive technique that requires minimal sample preparation as it does not require the addition of any foreign materials for irradiation. Limitations of this method include the fact that elements such as sulphur, lead and cadmium cannot be determined accurately, as well as that INAA is more expensive than many other methods. In addition, to use this method an optimal loading of $>100 \mu\text{g}/\text{cm}^2$ is generally required (Gordon *et al.*, 1984). Analysis by INAA is compatible with sampling by high-volume, dichotomous and Partisol samplers.

6.3.7 Alternative Analytical Methods

There have been several reports of Energy Dispersive X-Ray (EDX) Spectrometry being used in conjunction with Scanning Electron Microscopy (SEM) (Linton *et al.*, 1980; Casuccio and Janocko, 1981; Shaw, 1983; Post and Buseck, 1984; Saucy *et al.*, 1987; Anderson *et al.*, 1988; Dzubay and Mamane, 1989; Hamilton *et al.*, 1994). Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) Spectrometry uses a computer-controlled scanning electron microscope equipped with image analysis software to determine the size and shape of a moderate number of particles and EDX to provide qualitative and a moderately sensitive quantitative elemental analysis in a similar manner as XRF analysis. Generally, low loadings are required to employ this technique, therefore, a low-flow device such as dichotomous, Partisol or the MiniVol samplers should be used.

The primary advantage of the SEM-EDX technique is the ability to characterize individual particles both chemically and physically. The Expert Panel on the U.S. Environmental Protection Agency PM_{2.5} Chemical Speciation Network has recommended using the SEM-EDX

for analysis of air filters (U.S. EPA, 1999b). The panel found that microscopic techniques could be used to characterize both the morphology and the chemical composition of individual particles (Koutrakis, 1998). The disadvantages of the SEM-EDX technique include poor quantitative sensitivity (Linton *et al.*, 1980) and practical difficulties such as excessive time for a representative analysis and the occurrence of both particle damage and compositional changes during analysis (Post and Buseck, 1984). In addition, the EDX technique often results in potential spectral interferences requiring complex spectral deconvolution procedures.

Advances in microscopic techniques, particularly in sample analysis software, now permit collection of reasonably large datasets of individual particle morphology and composition. This technology has helped to overcome the sometimes-problematic issue of only being able to analyze a moderate number of particles in a reasonable time frame with the conventional SEM-EDX technique. To illustrate this point, an increasing number of studies in recent years (Rojas *et al.*, 1990; Van Borm *et al.*, 1989; Xhoffer *et al.*, 1991) have employed electron probe microanalysis to analyze individual particles. However, these technologies are very expensive, still in the developmental phase and are not readily available.

Table 8 Method Advantages and Disadvantages

Method	Advantages	Disadvantages
Sampling Methods		
<i>Hi-Vol Sampler</i>	Reference method	Many interferences
	Well documented applications	Cannot sample fine fraction
	Collects a substantial amount of material	Not compatible with some analytical techniques
	Lower concentrations of metals can be detected	Inconvenient
<i>Dichotomous Sampler</i>	Reference method	Low loadings
	Collects two size fractions	Requires a higher concentration
	Allows use of various filter media	
<i>Partisol Sampler</i>	Simple and convenient	Low loadings
	Allows use of various filter media	Requires a higher concentration
	Simple, convenient and inexpensive	Low loadings
<i>Mini-Vol Sampler</i>	Allows use of various filter media	Requires a higher concentration
		Limited documented applications
Analytical Methods:		
<i>Flame Atomic Absorption Spectroscopy</i>	Easy to use	Higher concentration required
	Extensive applications	Sample dissolution is required
	Low detection limits	One element at a time
	Well documented applications	Limited working range sample
<i>Graphite Furnace Atomic Absorption Spectroscopy</i>	Lower detection limits than FAA	Low sample throughput
		One element at a time
		More operator skill
		Sample dissolution is required
<i>X-Ray Fluorescence Spectroscopy</i>	Multi-element	Standard/sample must match closely
	Non-destructive	Matrix offsets and background
	Minimal sample preparation	impurities may be a problem
	Multi-elemental	More expensive (~120K)
<i>Inductively Coupled Plasma Spectroscopy</i>	High sample throughput	Sample dissolution is required
	Well documented applications	Other elements can interfere
	Intermediate operator skill	
	Linear range over 5 orders of magnitude	
<i>Inductively Coupled Plasma/Mass Spectroscopy</i>	Multi-elemental	Most expensive (~250K)
	Low concentrations	Limited documented applications
	Isotopic analysis	Sample dissolution is required
<i>Proton Induced X-Ray Emission Spectroscopy</i>	Intermediate operator skills	
	Multi-element	Standard/sample must match closely
	Non-destructive	Matrix offsets and background
	Minimal sample preparation	impurities may be a problem
	Multi-element	Some elemental interferences
<i>Instrumental Neutron Activation Analysis Spectroscopy</i>	Non-destructive	Standard sample matrix corrections
	Minimal sample preparation	Required access to research nuclear reactor
	Detection limit to ppt range	
	High sample throughput	
	Well documented applications	
<i>Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy</i>	Chemical and physical characterization	Poor sensitivity
	Non-destructive	Time consuming
	Minimal sample preparation	Limited documented applications

7.0 AMBIENT GUIDELINES

Current and/or recommended and proposed ambient guidelines of other jurisdictions in Canada, United States and elsewhere were reviewed for arsenic. Details about guidelines that exist for each jurisdiction reviewed are presented in tabular format in Section 7.1. In general, all jurisdictions have common uses for their guidelines. These uses may include:

- reviewing permit applications for sources that emit air pollutants to the atmosphere,
- investigating accidental releases or community complaints about adverse air quality for the purpose of determining follow-up or enforcement activity,
- determining whether to implement temporary emission control actions under persistent adverse air quality conditions of a short-term nature.

7.1 Arsenic Air Quality Guidelines

Air quality guidelines for arsenic are summarized in Table 9. The two principal approaches by which guidelines are developed include:

- Using an occupational exposure level (OEL) and dividing it by safety or adjustment factors. The most common OEL used by most state agencies is the 8-hour threshold limit value (TLV) of $10 \mu\text{g}/\text{m}^3$ adopted by the American Conference of Governmental Industrial Hygienists (ACGIH). The safety or adjustment factors are intended to account for issues such as: differences between eight-hour exposures in the workplace and continuous 24-hour environmental exposures, increased susceptibility of some people in the general population versus the relatively healthy worker, and uncertainty in the margin of safety provided in an occupational exposure limit.
- Using carcinogenic risk assessment procedures. Pre-existing cancer risk assessments performed by others (e.g. US EPA Integrated Risk Information System summary data) are used to establish ambient air levels based on acceptable levels of lifetime cancer risk, such as one in 100,000 (10^{-5}).

For the most part, the guidelines in Table 9 are derived based on US EPA's inhalation unit risk factor of $4.3\text{E-}03$ per $\mu\text{g}/\text{m}^3$ or the American Conference of Governmental Industrial Hygienists (ACGIH) 8-hour time weighted average occupational exposure limit (OEL) of $10 \mu\text{g}/\text{m}^3$. These guidelines apply to averaging times of 1-hour to annual (continuous exposure duration).

7.1.1 *Canada*

The Ontario Ministry of the Environment (MOE) adopted an Ambient Air Quality Criterion (AAQC) of $0.3 \mu\text{g}/\text{m}^3$ as a 24-hour guideline. Ontario MOE uses a maximum point of impingement (POI) guideline of $1 \mu\text{g}/\text{m}^3$ based on a 30-minute averaging time to review permit applications for stationary sources that emit arsenic to the atmosphere.

Agency: Ontario Ministry of the Environment (OME).
Air Quality Guideline: Ambient Air Quality Criterion (AAQC) = $0.3 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Limiting effect based on health.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: Used by Ontario Ministry of Environment (OME) to represent human health or environmental effect-based values not expected to cause adverse effects based on continuous exposure.
Additional Comments: AAQC <u>is not</u> used by OME to permit stationary sources that emit arsenic to the atmosphere. A "point of impingement" standard is used to for permitting situations.
Reference and Supporting Documentation: Ontario Ministry of the Environment. 1999. Summary of Point Of Impingement Standards, Point Of Impingement Guidelines, and Ambient Air Quality Criteria (AAQC). Standards Development Branch, Ontario Ministry of the Environment, Toronto, ON. November 1999. 12 pp.

Agency:
Ontario Ministry of the Environment (OME).
Air Quality Guideline:
Maximum point of impingement (POI) Guideline = $1 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies:
30-minute averaging time.
Basis for Development:
Limiting effect based on health.
Date Guideline Developed:
Unknown.
How Guideline is Used in Practice:
Used by OME to review permit applications for stationary sources that emit arsenic to the atmosphere.
Additional Comments:
n/a
Reference and Supporting Documentation:
Ontario Ministry of the Environment. 1999. Summary of Point Of Impingement Standards, Point Of Impingement Guidelines, and Ambient Air Quality Criteria (AAQC). Standards Development Branch, Ontario Ministry of the Environment, Toronto, ON. November 1999. 12 pp.

Agency:
US Agency for Toxic Substances and Disease Registry (ATSDR).
Air Quality Guideline:
ATSDR does not have an ambient air guideline for this chemical.
Averaging Time To Which Guideline Applies:
n/a
Basis for Development:
n/a
Date Guideline Developed:
n/a
How Guideline is Used in Practice:
n/a
Additional Comments:
n/a
Reference and Supporting Documentation:
Agency for Toxic Substances and Disease Registry (ATSDR). 2003. Minimal Risk Levels (MRLs) for Hazardous Substances. ATSDR, Public Health Service, US Department of Health and Human Services. Atlanta, GA. Available at: http://www.atsdr.cdc.gov/mrls.html (accessed 22 January 2003).

Agency: US Environmental Protection Agency (EPA).
Air Quality Guideline: Risk specific concentration (RsC) corresponding to 1 in 100,000 risk = $0.002 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies: Continuous exposure (daily exposure over a lifetime).
Basis for Development: The RsC corresponding to 1 in 100,000 risk (risk criteria used in Alberta) was derived using data from evidence of lung cancer in males exposed in the workplace (smelters) and US EPA's inhalation unit risk factor of $4.3\text{E}-03$ per $\mu\text{g}/\text{m}^3$.
Date Guideline Developed: Last revised in 1988.
How Guideline is Used in Practice: The risk specific concentration (RsC) is not used for any specific purposes by US EPA and is shown here to illustrate an exposure concentration in air associated with an inhalation unit risk factor derived by US EPA and a 1 in 100,000 lifetime cancer risk.
Additional Comments: The Integrated Risk Information System (IRIS) is prepared and maintained by the US EPA. IRIS is an electronic database containing information on human health effects that may result from exposure to various chemicals in the environment.
Reference and Supporting Documentation: US Environmental Protection Agency. Integrated Risk Information System. http://www.epa.gov/iris/ (accessed 22 January 2003).

Agency: California Environmental Protection Agency (Cal EPA).
Air Quality Guideline: Acute reference exposure level (REL) = 0.19 $\mu\text{g}/\text{m}^3$ [4-hour averaging time]. Chronic reference exposure level (REL) = 0.03 $\mu\text{g}/\text{m}^3$ [continuous (daily) exposure over a lifetime].
Averaging Time To Which Guideline Applies: See above.
Basis for Development: The acute and chronic RELs represent toxicity values recently adopted by Cal EPA Office of Environmental Health Hazard Assessment (OEHHA). Basis for the acute REL was decreased fetal weight in mice maternal exposed by inhalation for 4 hours on gestation days 9, 10, 11, and 12. A 4-hour exposure concentration representing a LOAEL of 0.26 mg/m^3 As_2O_3 (0.19 $\text{mg As}/\text{m}^3$) was adjusted with uncertainty factors (10 for the LOAEL, 10 for interspecies, and 10 for intraspecies) to estimate an acute REL of 0.19 $\mu\text{g}/\text{m}^3$ after rounding. The basis for development of the chronic REL is limited other than that it is based on cardiovascular, developmental and nervous system effects.
Date Guideline Developed: Acute REL – March 1999. Chronic REL – January 2001.
How Guideline is Used in Practice: Acute and chronic RELs are for use in facility health risk assessments conducted for the AB 2588 Air Toxics “Hot Spots” Program.
Additional Comments: n/a
Reference and Supporting Documentation: California Environmental Protection Agency (Cal EPA). 1999. Determination of Acute Reference Exposure Levels for Airborne Toxicants. Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section, Cal EPA. Oakland, CA. March 1999. California Office of Environmental Health Hazard Assessment (OEHHA)/Air Resources Board (ARB). 2001. Approved Chronic Reference Exposure Levels and Target Organs. Table 3 (last updated 13 September 2001). Available at: www.arb.ca.gov/toxics/healthval/chronic.pdf (accessed 22 January 2003).

Agency:
Louisiana Department of Environmental Quality (DEQ).
Air Quality Guideline:
Ambient air standard (AAS) for toxic air pollutants = $0.02 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies:
Annual average.
Basis for Development:
Not stated. However, $0.02 \mu\text{g}/\text{m}^3$ represents a risk specific concentration (RsC) corresponding to 1 in 10,000 risk using US EPA data.
Date Guideline Developed:
Not stated.
How Guideline is Used in Practice:
AASs are used by Louisiana DEQ to review permit applications for stationary sources that emit arsenic to the atmosphere.
Additional Comments:
n/a
Reference and Supporting Documentation:
Louisiana Administrative Code (LAC). Title 33 Environmental Quality, Part III Air, Chapter 51. Comprehensive Toxic Air Pollutant Emission Control Program. Louisiana Department of Environmental Quality. Baton Rouge, LA.

Agency: Massachusetts Department of Environmental Protection (DEP).
Air Quality Guideline: Threshold Effects Exposure Limit (TEL) = 0.0005 $\mu\text{g}/\text{m}^3$ [24-hour averaging time]. Allowable Ambient Limit (AAL) = 0.0002 $\mu\text{g}/\text{m}^3$ [annual average].
Averaging Time To Which Guideline Applies: See above.
Basis for Development: TEL: Unknown. AAL: Not stated. However, 0.0002 $\mu\text{g}/\text{m}^3$ represents a risk specific concentration (RsC) corresponding to 1 in 1,000,000 risk using US EPA data.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: Information could not be obtained to identify how the guideline is used in practice, but it is expected that the guideline is used in some manner to meet state level permitting
Additional Comments: n/a
Reference and Supporting Documentation: Massachusetts Department of Environmental Protection (DEP). 1995. Revised air guidelines [updated list of 24-hour average Threshold Effects Exposure Limit (TEL) values and annual average Allowable Ambient Limit (AAL) values]. Massachusetts DEP, Boston, MA. 6 December 1995. Memorandum available at: http://www.state.ma.us/dep/ors/files/aallist.pdf (accessed 22 January 2003).

Agency:
Michigan Department of Environmental Quality (DEQ).
Air Quality Guideline:
Initial risk screening level (IRSL) = 0.0002 $\mu\text{g}/\text{m}^3$ [annual averaging time].
Secondary risk screening level (SRSL) = 0.002 $\mu\text{g}/\text{m}^3$ [annual averaging time].
Averaging Time To Which Guideline Applies:
See above.
Basis for Development:
The IRSL and SRSL are based on US EPA's inhalation unit risk factor of 4.3E-03 per $\mu\text{g}/\text{m}^3$ corresponding to 1 in 1,000,000 and 1 in 100,000 risk, respectively.
Date Guideline Developed:
1994.
How Guideline is Used in Practice:
There are two basic requirements of Michigan air toxic rules. First, each source must apply the best available control technology for toxics (T-BACT). After the application of T-BACT, the emissions of the toxic air contaminant cannot result in a maximum ambient concentration that exceeds the applicable health based screening level for carcinogenic effects.
Additional Comments:
There are two health-based screening levels for chemical treated as carcinogens by Michigan DEQ: the initial risk screening level (IRSL) – based on an increased cancer risk of one in one million, and the secondary risk screening level (SRSL) – based on as an increased cancer risk of 1 in 100,000.
Reference and Supporting Documentation:
Michigan Administrative Code (MAC). Air Pollution Control Rules. Part 2 Air Use Approval, R 336.1201 - 336.1299. Air Quality Division, Department of Environmental Quality. Lansing, MI.

Agency: New Hampshire Department of Environmental Services (DES).
Air Quality Guideline: 24-hour ambient air limit (AAL) = $0.036 \mu\text{g}/\text{m}^3$. Annual ambient air limit (AAL) = $0.024 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies: See above.
Basis for Development: The AALs were developed in the following manner: 24-hour Ambient Air Limit – The American Conference of Governmental Industrial Hygienists (ACGIH) 8-hour time weighted average occupational exposure limit (OEL) of $0.01 \text{ mg}/\text{m}^3$ is divided by a safety factor (SF) of 100 and a time adjustment factor (TAF) of 2.8. Annual Ambient Air Limit – The American Conference of Governmental Industrial Hygienists (ACGIH) 8-hour time weighted average occupational exposure limit (OEL) of $0.01 \text{ mg}/\text{m}^3$ is divided by a safety factor (SF) of 100 and a factor of 4.2.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: AALs are used by New Hampshire DES to review permit applications for sources that emit arsenic to the atmosphere. Sources are regulated through a statewide air permitting system and include any new, modified or existing stationary source, area source or device.
Additional Comments: n/a
Reference and Supporting Documentation: New Hampshire Administrative Rule, Chapter Env-A 1400. Regulated Toxic Air Pollutants. New Hampshire Department of Environmental Services, Concord, NH.

Agency:
New Jersey Department of Environmental Protection (DEP).
Air Quality Guideline:
Applicants are required to carry out a risk assessment in conjunction with applying for an air pollution control pre-construction permit. In the case of arsenic, the US Environmental Protection Agency inhalation unit risk factor of $4.3E-03$ per $\mu\text{g}/\text{m}^3$ is used to calculate a lifetime cancer risk for sources that emit arsenic to the atmosphere.
Averaging Time To Which Guideline Applies:
Continuous (daily) exposure over a lifetime.
Basis for Development:
Based on US EPA Integrated Risk Information System (IRIS) data.
Date Guideline Developed:
December 1994.
How Guideline is Used in Practice:
Used by New Jersey DEP to review permit applications for sources that emit arsenic to the atmosphere.
Additional Comments:
n/a
Reference and Supporting Documentation:
New Jersey Administrative Code (NJAC). Title 7, Chapter 27, Subchapter 8. Permits and Certificates for Minor Facilities (and Major Facilities without an Operating Permit). New Jersey Department of Environmental Protection. Trenton, NJ.
New Jersey Department of Environmental Protection. 1994. Technical Manual 1003. Guidance on Preparing a Risk Assessment for Air Contaminant Emissions. Air Quality Permitting Program, Bureau of Air Quality Evaluation, New Jersey Department of Environmental Protection. Trenton, NJ. Revised December 1994.

Agency:
North Carolina Department of Environment and Natural Resources (ENR).
Air Quality Guideline:
Acceptable ambient level (AAL) = $0.00023 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies:
Annual average.
Basis for Development:
Not stated. Although not stated, the AAL was likely derived by using an increased cancer risk of one in 1,000,000 (10^{-6}) and the US EPA's inhalation unit risk factor of $4.3\text{E-}03$ per $\mu\text{g}/\text{m}^3$.
Date Guideline Developed:
1990.
How Guideline is Used in Practice:
A facility emitting arsenic must limit its emissions so that the resulting modeled ambient levels at the property boundary remain below the health-based acceptable ambient level (AAL).
Additional Comments:
n/a
Reference and Supporting Documentation:
North Carolina Administrative Code (NCAC). North Carolina Air Quality Rules 15A NCAC 2D.1100 – Air Pollution Control Requirements (Control of Toxic Air Pollutants). North Carolina Department of Environment and Natural Resources. Raleigh, NC.
North Carolina Administrative Code (NCAC). North Carolina Air Quality Rules 15A NCAC 2Q.0700 – Air Quality Permit Procedures (Toxic Air Pollutant Procedures). North Carolina Department of Environment and Natural Resources. Raleigh, NC.

Agency: Ohio Environmental Protection Agency (EPA).
Air Quality Guideline: Maximum acceptable ground-level concentration (MAGLC) = $0.24 \mu\text{g}/\text{m}^3$ (proposed).
Averaging Time To Which Guideline Applies: 1-hour averaging time.
Basis for Development: $\text{MAGCL} = \frac{\text{TLV}}{10} \times \frac{8 \text{ hr}}{24 \text{ hr}} \times \frac{5 \text{ d}}{7 \text{ d}} = \frac{\text{TLV}}{42}.$ The TLV is the ACGIH 8-hour time weighted average occupational exposure limit (OEL) of $0.01 \text{ mg}/\text{m}^3$. The TLV is adjusted by a safety factor of 10 to take into account greater susceptibility of the general population in comparison to healthy workers. The 8/24 and the 5/7 multipliers are used to relate the exposure to longer than 40-hour time periods and ascertain that the individual's total exposure will be no greater than that allowed by the TLV.
Date Guideline Developed: January 1994 (proposed).
How Guideline is Used in Practice: Used by Ohio EPA to review permit applications for sources that emit arsenic to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Ohio Environmental Protection Agency (EPA). 2003. Review of New Sources of Toxic Emissions. Air Toxics Unit, Division of Air Pollution Control, Ohio EPA. Columbus, OH. 11 pp (available at: http://www.epa.state.oh.us/dapc/atu/atu.html , accessed 22 January 2003). Ohio Environmental Protection Agency (Ohio EPA). 1994. Review of New Sources of Air Toxic Emissions. Proposed for Public Comment. Division of Air Pollution Control, Ohio EPA. Columbus, OH. January 1994. 31 pp.

Agency:
Oklahoma Department of Environmental Quality (DEQ).
Air Quality Guideline:
Maximum acceptable ambient concentration (MAAC) = $2 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies:
24-hour averaging time.
Basis for Development:
Unknown.
Date Guideline Developed:
Not stated.
How Guideline is Used in Practice:
MAACs are used by Oklahoma DEQ to review permit applications for sources that emit arsenic to the atmosphere.
Additional Comments:
n/a
Reference and Supporting Documentation:
Oklahoma Administrative Code (OAC). Title 252. Chapter 100. Air Pollution Control. 100:252-41 - Control of Emission of Hazardous and Toxic Air Contaminants. Oklahoma Department of Environmental Quality. Oklahoma City, OK.
Oklahoma Department of Environmental Quality (DEQ). 2002. Air Toxics Partial Listing [maximum acceptable ambient concentrations (MAAC) for air toxics]. Oklahoma City, OK. Available at: http://www.deq.state.ok.us/AQDNew/toxics/listings/pollutant_query_1.html (accessed 23 January 2003).

Agency: Rhode Island Department of Environmental Management (DEM).
Air Quality Guideline: Acceptable ambient level (AAL) = 0.0002 $\mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies: Annual average.
Basis for Development: Not stated. Although not stated, the AAL was likely derived by using an increased cancer risk of one in 1,000,000 (10^{-6}) and the US EPA's inhalation unit risk factor of 4.3E-03 per $\mu\text{g}/\text{m}^3$.
Date Guideline Developed: Unknown.
How Guideline is Used in Practice: AALs are used by Rhode Island DEM to review permit applications for sources that emit arsenic to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Rhode Island Department of Environmental Management. 1992. Air Pollution Control Regulation No. 22. Division of Air and Hazardous Materials, Rhode Island Department of Environmental Management. Providence, RI. Amended 19 November 1992.

Agency: Texas Commission on Environmental Quality (CEQ) – formerly Texas Natural Resource Conservation Commission (TRNCC).
Air Quality Guideline: Short-term effects screening level (ESL) = $0.1 \mu\text{g}/\text{m}^3$. Long-term effects screening level (ESL) = $0.01 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies: 1-hour averaging time for short-term ESL. Annual averaging time for long-term ESL.
Basis for Development: Short-term Effects Screening Level – The ACGIH TLV – 8-hour time weighted average occupational exposure limit (OEL) of $0.01 \text{ mg}/\text{m}^3$ – is divided by a safety factor of 100. Long-term Effects Screening Level – The ACGIH TLV – 8-hour time weighted average occupational exposure limit (OEL) of $0.01 \text{ mg}/\text{m}^3$ – is divided by a safety factor of 1000.
Date Guideline Developed: Not stated.
How Guideline is Used in Practice: ESLs are used to evaluate the potential for effects to occur as a result of exposure to concentrations of constituents in air. ESLs are based on data concerning health effects, odor nuisance potential, effects with respect to vegetation, and corrosion effects. They are not ambient air standards. If predicted or measured airborne levels of a chemical do not exceed the screening level, adverse health or welfare effects would not be expected to result. If ambient levels of constituents in air exceed the screening levels, it does not necessarily indicate a problem, but rather, triggers a more in-depth review.
Additional Comments: n/a
Reference and Supporting Documentation: Texas Natural Resource Conservation Commission (TNRCC) 2001. Toxicology & Risk Assessment (TARA) Section Effects Screening Levels. http://www.tnrcc.state.tx.us/permitting/tox/index.html (accessed 23 January 2003).

Agency:
Vermont Agency of Natural Resources (ANR).
Air Quality Guideline:
Hazardous ambient air standard (HAAS) = $0.00023 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies:
Annual Average.
Basis for Development:
The HAAS for known or suspected carcinogens (such as arsenic) is set at a level which represents an excess risk of one additional cancer case per one million exposed population (10^{-6}) assuming constant exposure at the HAAS concentration for a lifetime. Although not stated, it was derived by using US EPA's inhalation unit risk factor of $4.3\text{E}-03$ per $\mu\text{g}/\text{m}^3$.
Date Guideline Developed:
Not stated.
How Guideline is Used in Practice:
HAASs are used by Vermont ANR to review permit applications for stationary sources that emit arsenic to the atmosphere.
Additional Comments:
n/a
Reference and Supporting Documentation:
Vermont Air Pollution Control Regulations. 2001. State of Vermont Agency of Natural Resources. Air Pollution Control Division. Waterbury, VT. 29 November 2001. 187 pp.

Agency:
Washington State Department of Ecology (DOE).
Air Quality Guideline:
Acceptable source impact level (ASIL) = $0.00023 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies:
Annual average.
Basis for Development:
The ASIL for arsenic is a risk-based acceptable source impact level that may cause an increased cancer risk of one in one million (10^{-6}) using US EPA's inhalation unit risk factor of $4.3\text{E-}03$ per $\mu\text{g}/\text{m}^3$.
Date Guideline Developed:
Unknown.
How Guideline is Used in Practice:
ASILs are used by Washington State DOE to review permit applications for sources that emit arsenic to the atmosphere.
Additional Comments:
n/a
Reference and Supporting Documentation:
Washington Administrative Code (WAC). Chapter 173-460 WAC. Controls For New Sources Of Toxic Air Pollutants. Washington State Department of Ecology. Olympia, WA.

Agency: Wisconsin Department of Natural Resources (DNR).
Air Quality Guideline: Ambient air concentration (AAC) = $0.24 \mu\text{g}/\text{m}^3$ (proposed).
Averaging Time To Which Guideline Applies: 24-hour averaging time.
Basis for Development: Unknown. However the AAC is equivalent to the ACGIH TLV – 8-hour time weighted average occupational exposure limit (OEL) of $0.01 \text{ mg}/\text{m}^3$ – is divided by a safety factor of 42 and rounded. The factor of 42 is a common adjustment representing a safety factor of 10 and 8/24 and 5/7 multipliers to convert 8-hour per 24-hour day and 5-day per 7-day week occupational exposures to continuous exposures.
Date Guideline Developed: Not stated.
How Guideline is Used in Practice: AACs are used by Wisconsin DNR to review permit applications for sources that emit arsenic to the atmosphere.
Additional Comments: n/a
Reference and Supporting Documentation: Wisconsin Administrative Code (WAC). Air Pollution Control Rules. Chapter NR 445. Control of Hazardous Pollutants. Wisconsin Department of Natural Resources. Madison WI.

Agency:
New Zealand Ministry for the Environment and New Zealand Ministry of Health.
Air Quality Guideline:
Air guideline for protecting human health and wellbeing = $0.0055 \mu\text{g}/\text{m}^3$ (proposed).
Averaging Time To Which Guideline Applies:
Annual average.
Basis for Development:
Based on risk assessment.
Date Guideline Developed:
2000.
How Guideline is Used in Practice:
Air guidelines represent proposed guideline values for air-shed management.
Additional Comments:
n/a
Reference and Supporting Documentation:
New Zealand Ministry for the Environment and Ministry of Health (New Zealand). 2000. Proposals for Revised and New Ambient Air Quality Guidelines. Discussion Document. Air Quality Technical Report No 16. Prepared by the Ministry for the Environment and the Ministry of Health. December 2000. 79 pp.

Agency:
The Netherlands National Institute of Public Health and the Environment (RIVM)
Air Quality Guideline:
Tolerable concentration in air (TCA) = 1 $\mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies:
Annual average.
Basis for Development:
RIVM (2001) reported that the most critical effect after chronic inhalation exposure of humans was lung cancer in humans. RIVM (2001) reported that the LOAEC (lowest observed adverse effects concentration) for trivalent arsenic for this effect is 10 $\mu\text{g}/\text{m}^3$. An extrapolation factor of 10 was used to account for variation in susceptibility of humans to derive a TCA of 1 $\mu\text{g}/\text{m}^3$. The TCA is proposed for both trivalent and pentavalent forms of arsenic.
Date Guideline Developed:
2001.
How Guideline is Used in Practice:
TCAs are intervention values used to make decisions regarding air contamination. The TCA represents an air concentration that humans can inhale during their lifetime without resultant adverse health effects.
Additional Comments:
n/a
Reference and Supporting Documentation:
The Netherlands National Institute of Public Health and the Environment (RIVM). 2001. Re-evaluation of human-toxicological maximum permissible risk levels. RIVN Report 711701 025. RIVN, Bilthoven, The Netherlands. March 2001. 297 pp.

Agency: World Health Organization (WHO)
Air Quality Guideline: Ambient air guidance value recommended for general population corresponding to an excess lifetime risk level of 1 in 100,000 = $0.0066 \mu\text{g}/\text{m}^3$.
Averaging Time To Which Guideline Applies: Continuous (daily) exposure over a lifetime.
Basis for Development: The ambient air guidance value for arsenic based an increased cancer risk of 1 in 100,000 (10^{-5}) was derived by using an inhalation unit risk factor of $1.51\text{E}-03$ per $\mu\text{g}/\text{m}^3$.
Date Guideline Developed: 2000.
How Guideline is Used in Practice: The guideline is intended to provide background information and guidance to governments in making risk management decisions, particularly in setting standards.
Additional Comments: n/a
Reference and Supporting Documentation: World Health Organization (WHO). 2000. Air Quality Guidelines for Europe, 2nd Edition. WHO Regional Publications, European Series, No. 91. WHO Regional Office for Europe, Copenhagen. 273 pp

7.1.2 *United States*

No health-based criteria exist for arsenic from the US Agency for Toxic Substances and Disease Registry.

The US EPA used data from evidence of lung cancer in males exposed in the workplace (smelters) to derive an inhalation unit risk factor of $4.3\text{E-}03$ per $\mu\text{g}/\text{m}^3$. The inhalation unit risk factor is intended for use by US EPA staff in risk assessments, decision-making and regulatory activities. Eight of the US agencies reviewed – those in Louisiana, Massachusetts, Michigan, New Jersey, North Carolina, Rhode Island, Vermont, and Washington – have adopted or derived their annual average values from the US EPA inhalation unit risk factor of $4.3\text{E-}03$ per $\mu\text{g}/\text{m}^3$.

Four state agencies – those in New Hampshire, Ohio, Texas, and Wisconsin – use the ACGIH 8-hour TLV ($10 \mu\text{g}/\text{m}^3$) in development of various ambient guidelines for arsenic.

7.1.3 *International Agencies*

The New Zealand Ministry of Environment and Ministry of Health recently proposed an air guideline for arsenic of $0.0055 \mu\text{g}/\text{m}^3$ as an annual average. The Netherlands National Institute of Public Health and the Environment (RIVM, 2001) recently adopted a tolerable concentration in air of $1 \mu\text{g}/\text{m}^3$ as an annual average for arsenic. The World Health Organization (WHO, 2000) recommended an ambient air guidance value of $0.0066 \mu\text{g}/\text{m}^3$ for the general population corresponding to an excess lifetime risk level of 1 in 100,000. The guideline is intended to provide background information and guidance to governments in making risk management decisions, particularly in setting standards.

Table 9 Summary of Air Quality Guidelines for Arsenic

Agency	Guideline Title	Guideline Value [$\mu\text{g}/\text{m}^3$] Averaging Time:			
		1-hour	4-hour	24-hour	annual
Ontario MOE	Ambient Air Quality Criterion (AAQC): Maximum point of impingement (POI) Guideline (30-min. averaging time): Risk specific concentration (RsC): ¹ Acute reference exposure level (REL): Chronic REL: Ambient air standard (AAS): Threshold Effects Exposure Limit (TEL): Allowable Ambient Limit (AAL): Initial risk screening level (IRSL): Secondary risk screening level (SRL): 24-hour ambient air limit (AAL): Annual AAL: Risk assessment approach is used - Risk specific concentration (RsC): ¹ Acceptable ambient level (AAL): Maximum acceptable ground-level concentration (MAGLC): ² Maximum acceptable ambient concentration (MAAC): Acceptable ambient level (AAL):	1	0.19	0.3	0.002 0.03 0.02 0.0002 0.0002 0.002 0.024 0.0023 0.00023
US EPA					
California EPA					
Louisiana DEQ					
Massachusetts DEP					
Michigan DEQ					
New Hampshire DES					
New Jersey DEP					
North Carolina ENR					
Ohio EPA		0.24			
Oklahoma DEQ					
Rhode Island DEM					
Texas Commission on Environmental Quality					
Vermont ANR		0.1			0.01 0.00023 0.00023
Washington DOE					
Wisconsin DNR					
New Zealand MOE				0.24	0.0055
The Netherlands (RIVM)					1
World Health Organization					0.0066

¹ The RsC is not used for any specific purposes by the respective agency. It is shown here to illustrate an exposure concentration in air associated with an inhalation unit risk factor used by the agency and a 1 in 100,000 lifetime cancer risk (risk criteria used in Alberta).

² Proposed.

8.0 RISK CHARACTERIZATION

Risk characterization of an ambient air contaminant involves the integration and evaluation of several types of key information. Where it is undertaken for a site-specific situation, such as for the screening assessment of proposed industrial emissions of arsenic, quantitative approaches can be used. For ambient air exposures, this may involve taking measurements or using a computer dispersion model to estimate ambient ground-level concentrations of arsenic under different averaging times and making comparisons to safe levels of exposure (air quality guidelines).

For the general case, however, use of site-specific risk characterization approaches is limited unless a number of assumptions are made. The emission characteristics for sources of arsenic release to air in Alberta vary for point sources such as industrial emissions. In addition, meteorological dispersion conditions can vary from site to site. This variability is difficult to represent as a general case for quantitative assessment and the resulting risk characterization would have substantial uncertainty. As a result, a qualitative risk characterization approach is used to evaluate issues associated with arsenic in ambient air. The types of key information evaluated can include, but not be limited to:

- relevant chemical forms in air
- pathways by which exposure may occur
- relevant potential effects (impacts)

These issues are discussed further below.

8.1 Relevant Chemical Forms

Arsenic is present in the atmosphere mostly as a variable mixture of tri- and pentavalent species of inorganic arsenic, with the latter being predominant form. In the atmosphere, it exists as particulate matter, mostly as particles less than 2 μm in aerodynamic diameter. These particles are transported by wind and air currents until they return to the ground by wet or dry deposition.

8.2 Exposure Assessment

In considering the potential for inhalation exposure for humans, background levels of arsenic in community ambient air tend to be low. Greater variability in ambient levels of arsenic is expected near industrial point sources.

8.3 Toxicity Assessment

Occupational settings have shown that breathing high levels of inorganic arsenic may result in sore throats and irritated lungs, and it may also result in the development of some skin effects. The exposure level that produces these effects is uncertain, but it is probably above 100 $\mu\text{g}/\text{m}^3$ for a brief exposure (ATSDR, 2003). Another important issue is the ability of inhaled inorganic arsenic to increase the risk of lung cancer.

8.4 Characterization of Risk

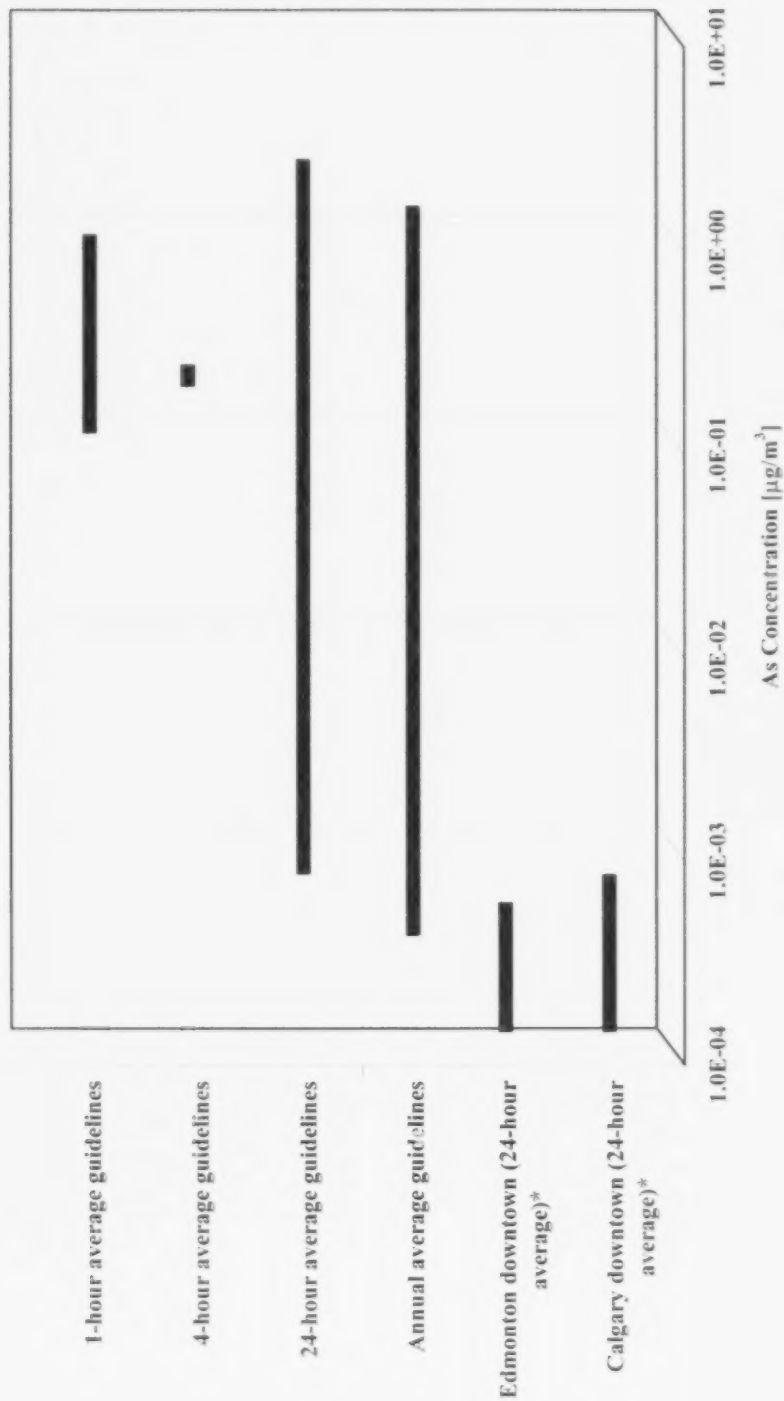
With respect to protection of the general population from inhalation exposure to arsenic and other air toxics released from industrial activities, acute (short-term) exposure situations tend only to receive attention from regulatory agencies during the permitting process. An example of this is the use of computer dispersion models to estimate ambient ground-level concentrations of air toxics emitted from an industry under short-term (e.g. hourly) averaging times and making comparisons to air quality criteria with similar averaging times to meet agency permitting requirements. The occurrences of elevated levels of air toxics in the environment are in general, short-term and probably a result of stagnant meteorological conditions (poor dispersion of air) or accidental releases from industry.

However, a common approach used by regulatory agencies to protect the general population from exposure to potentially toxic chemicals in the environment is through the development and use of media guidelines for chronic (long-term) exposure conditions. For example, this is evident in Canada with how potentially toxic chemicals are addressed in the Guidelines for Canadian Drinking Water Quality for drinking water protection (Health Canada, 2001) and Canadian Environmental Quality Guidelines for soil quality protection (CCME, 1999).

With respect to chronic (long-term) exposure conditions, an important concern to occupational health officials is the ability of inhaled inorganic arsenic to increase the risk of lung cancer. This has been seen mostly in workers exposed to arsenic at smelters, mines, and chemical factories, but also in residents living near smelters. The ability for much lower ambient levels of arsenic ($<<1 \mu\text{g}/\text{m}^3$) to increase the risk of lung cancer in the general population is much less certain. These low concentrations are much more representative of potential inhalation exposures to the general population. Nevertheless, many regulatory agencies adopt air quality guidelines for arsenic in order to protect humans.

The range of air quality guidelines proposed by various agencies for protection of human receptors is shown in Figure 1 for different averaging time periods. The data presented in Figure 1 were summarized from the previous section. Also shown in this figure is the range between the median and maximum 24-hour average concentration of arsenic in respirable particulate matter ($\text{PM}_{2.5}$) from air samples collected in central Edmonton and central Calgary from June 1991 to November 2000 (after AENV, 2003).

Urban settings – in which most air quality data are available for – are settings with higher metal concentrations in ambient air compared to rural settings (WHO, 2000). Figure 1 illustrates that the range between the median and maximum 24-hour average concentration of arsenic in $\text{PM}_{2.5}$ tends to be on the low side or less than air quality guidelines for protection of human receptors (irrespective of the averaging time).



* Range between the median and maximum 24-hour average concentration of arsenic in airborne PM_{2.5}

Figure 1 Range of Air Quality Guidelines for Arsenic Proposed by Various Agencies for Protection of Human Receptors

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